8 RADIOCHEMICAL DATA VERIFICATION AND VALIDATION

8.1 Introduction

The goal of the data collection process is to produce credible and cost-effective data to meet the needs of a particular project. The process can be divided into several stages, as illustrated in the data life cycle (Chapter 1). This chapter is the first of two chapters that address the assessment phase of the project. Because the efficiency and success of these assessment activities are heavily dependent on the completion of the preceding steps in the data collection process, especially the initial planning activity (Chapter 2), the integration of planning and assessment is discussed in Section 8.2 prior to presenting material on data verification and validation.

Data verification compares the material delivered by the laboratory to the requirements in the statement of work (SOW) and identifies problems, if present, that should be investigated during data validation. Data validation uses the outputs from data verification and compares the data produced with the measurement quality objectives (MQOs) and any other analytical process requirements contained in the analytical protocol specifications (APSs) developed in the planning process. The main focus of data validation is determining data quality relative to the project-specific MQOs. It may not be necessary in all instances to validate all project data. This chapter outlines a validation plan that specifies the data deliverables and data qualifiers to be assigned that will facilitate the data quality assessment. The project-specific data validation plan should establish a protocol that prioritizes the data to be validated. This is to eliminate unnecessarily strict requirements that commit scarce resources to the in-depth evaluation of data points with high levels of acceptable uncertainty. For example, results very much above or below an action level may not require rigorous validation, since relatively large measurement uncertainty would not affect the ultimate decision or action. Planners should also identify those samples or data sets that have less rigorous standards for data quality and defensibility.

This chapter presents suggested criteria to evaluate data and addresses the appropriate function and limits of radiochemical techniques and measurements. Since calibration is more efficiently evaluated as part of an audit, this chapter does not recommend that the complete calibration-support documentation be included as part of the data package. MARLAP recommends that calibration be addressed in a quality system and through an audit (Chapter 18, *Laboratory Quality Control*), although demonstration of calibration may be required as part of a project's deliverables. Detector calibration, self-absorption curves, and efficiencies should be addressed as part of the evaluation of

Contents

laboratories during the procurement process and continued during subsequent assessments (Chapter 7, *Evaluating Methods and Laboratories*). Availability and retention of calibration records are decisions that are project-specific, but should be clearly identified for contract clarity and to assure project completeness (i.e., customer needs met). External sources of information, such as performance evaluation sample results and internal laboratory control samples, provide useful interim information on calibration status and accuracy.

8.2 Data Assessment Process

Figure 1.1 in Chapter 1 graphically depicts the three phases of the data life cycle—planning, implementation, and assessment—and the associated activities and products of each phase. *While these activities are addressed in separate chapters in MARLAP, it should be emphasized that integration of planning, sampling, and analysis with subsequent data verification, data validation, and data quality assessment (DQA) is essential*.

This section reviews the data life cycle from the perspective of the assessment phase and focuses on those issues that have the potential to impact the quality and usability of the data. Section 8.2.1 addresses the development of the assessment procedures during project planning. Section 8.2.2 considers assessment needs for documentation and a quality system during implementation. Section 8.2.3 focuses on the assessment phase and addresses the interrelationship of the three assessment processes. This introduction to the data life cycle process emphasizes the importance of linkages among planning, implementation, and assessment.

8.2.1 Planning Phase of the Data Life Cycle

Directed project planning and the development of the associated data quality objectives (DQOs), MQOs, and other specifications for the project are reviewed in Chapters 2 and 3. *These chapters emphasize the need for planners to thoroughly define the assessment processes (i.e, verification, validation and data quality assessment) in sufficient detail that success or failure in meeting goals can be determined upon project completion.* MARLAP recommends that the assessment criteria of a project be established during the directed planning process and documented in the respective plans as part of the project plan documents. This requires the project planning team to develop detailed procedures for data verification, data validation, and data quality assessment, as well as identify the actual personnel who will perform assessment or the required qualifications and expertise of the assessors.

The development of these procedures during the directed planning process will increase the likelihood that the appropriate documentation will be available for assessment, and that those generating and assessing data will be aware of how the data will be assessed. A secondary advantage, which assessment plans have, is that prior to their completion, they often result in the detection of design flaws (e.g., lack of proper quality control [QC] samples, lack of a field audit)

that upon correction will result in the complete information necessary for the proper assessment of data usability.

The culmination of the planning process is documentation of the outputs of the directed planning process in the project plan documents. The project plan documents should capture the DQOs, MQOs, and the optimized data collection design (i.e., analytical protocol specifications, sampling and analysis plans, and standard operating procedures [SOPs]). The project plans should also include the assessment plans as discussed above, and describe the field, laboratory, safety, and quality assurance (QA) activities in sufficient detail that the project can be implemented as designed. Chapter 4 discusses guidance for writing project plan documents.

If the directed planning process, its outputs (DQOs, MQOs, optimized sampling and analysis designs), and associated assumptions are not documented well in project plan documents, the assessment phase will have difficulties evaluating the resulting data in terms of the project's objectives.

8.2.2 Implementation Phase of the Data Life Cycle

The project plans are executed during the implementation phase. Ideally, the plans would be implemented as designed, but due to errors, misunderstandings, the uncontrolled environments under which sampling is implemented, and matrix-specific issues that complicate sample handling and analysis, most project plans are not implemented without some deviation.

Understanding the realities of implementation, the assessment process, in particular the DQA process, will evaluate the project's implementation by considering: (a) if the plans were adequate to meet the project's DQOs, (b) if the plans were implemented as designed, and (c) if the plans as implemented were adequate to meet the project DQOs. MARLAP recommends that project objectives, implementation activities and QA/QC data be well documented in project plans, reports, and records, since the success of the assessment phase is highly dependent upon the availability of such information.

Documentation and record keeping during the planning and implementation phase of the data life cycle are essential to subsequent data verification, data validation, and data quality assessment. Thorough documentation will allow for a determination of data quality and data usability. *Missing documentation can result in uncertainty, and a lack of critical documentation (e.g., critical quality control results) can result in unusable data. The quality and usability of data can not be assessed if the supporting documentation is not available.*

8.2.2.1 Project Objectives

The DQOs, MQOs, and other specifications, requirements, and assumptions developed during the planning phase will influence the outcomes during the subsequent implementation and

assessment phases of the data life cycle. It is important that these objectives, specifications, requirements, and assumptions are well documented and available to those implementing the program so they can make informed decisions. This documentation is reviewed during the DQA process (see discussions of the reviews of project DQOs in Section 9.6.1.1, sampling plans in Section 9.6.2.1, and analysis plans in Section 9.6.3.1).

8.2.2.2 Documenting Project Activities

The assessment of data in terms of sampling and analytical MQOs requires an accurate record of QC sample data and compliance with specifications and requirements. If these records are missing or inadequate, then compliance with APSs, including the MQOs that were identified during the planning phase, will not be ascertainable and will raise questions regarding quality.

Additional documentation is required to assess compliance with plans and contracts, and to assess field and laboratory activities (e.g., compliance with SOPs) and the associated organizational systems (e.g., laboratory quality manual). This information is gleaned from the review of field and laboratory notebooks, deviation reports, chain-of-custody forms, verification reports, audit reports, surveillance reports, performance evaluation sample analyses, corrective action reports and reports to management that may identify deviations, contingencies, and quality problems. Assessment of these types of contemporaneous records allow for the assessment of data in the context of pertinent issues that may have arisen during project implementation.

Project records should be maintained for an agreed upon period of time, which should be specified in project plan documents. Record maintenance should comply with all regulatory requirements and parallel the useful life of the data for purposes of re-assessment as questions arise or for purposes of secondary data uses that were not originally anticipated.

8.2.2.3 Quality Assurance/Quality Control

To ensure that the data collection activity generates data of known quality, it is essential that the project plan documents specify the requirements for an appropriate quality system that is capable of implementing the quality controls and the quality assurance necessary for success.

The quality system will oversee the implementation of QC samples, documentation of QC sample compliance or noncompliance with MQOs, audits, surveillances, performance-testing sample analyses, corrective actions, quality improvement and reports to management. The documentation generated by these quality assurance activities and their outputs during project implementation will be a key basis for subsequent assessments and data usability decisions.

8.2.3 Assessment Phase of the Data Life Cycle

Assessment of environmental data currently consists of three separate and identifiable phases: data verification, data validation, and DQA. Verification and validation pertain to evaluation of analytical data. *Verification and validation are considered as two separate processes, but as the MARLAP recommended planning process is implemented, they may be combined.* DQA considers all sampling, analytical, and data handling details, external QA assessments, and other historical project data to determine the usability of data for decision-making.

Figure 8.1 is a graphical depiction of the assessment phase. Although the figure portrays a linear progression through the various steps, and from verification and validation to data quality

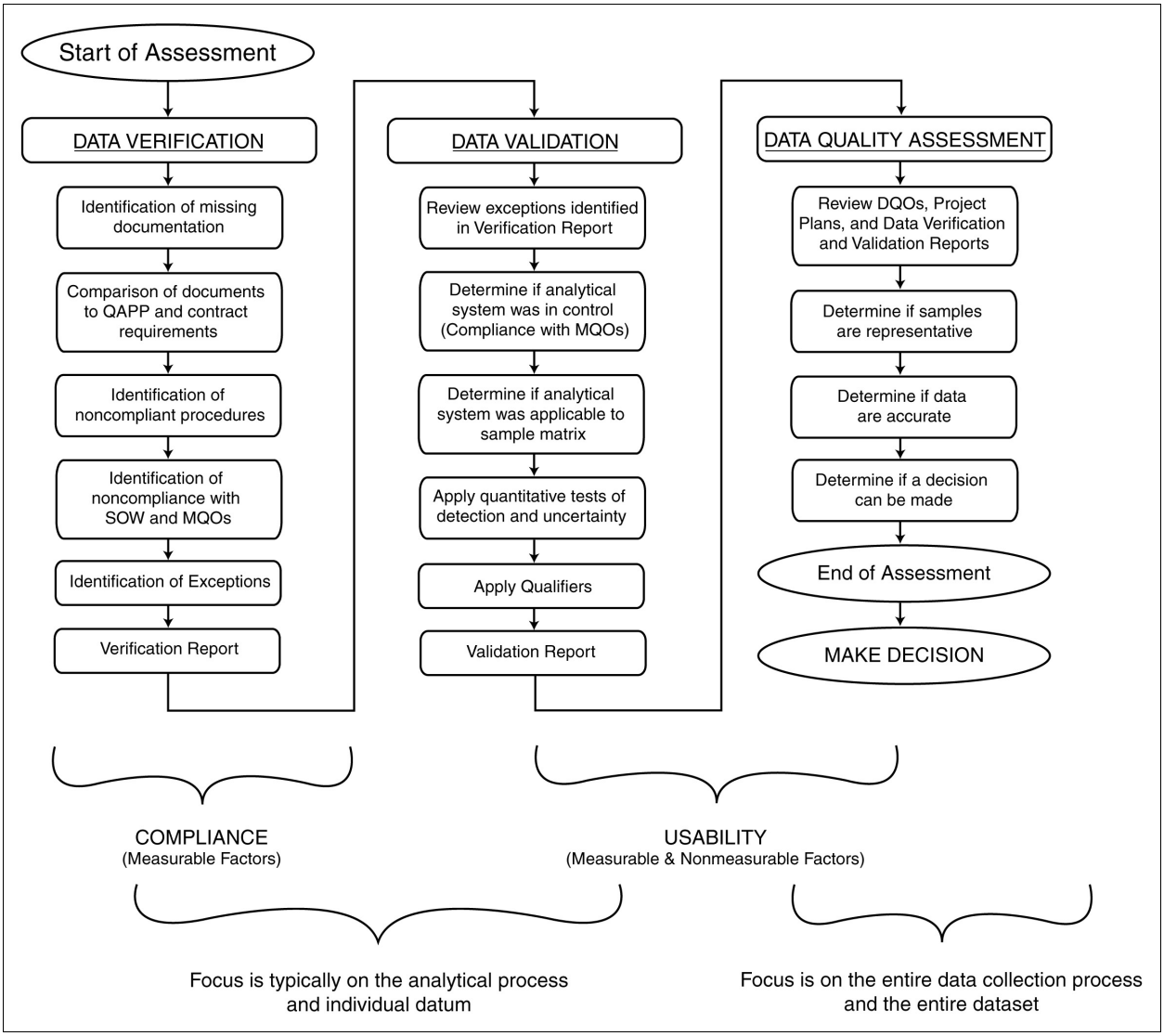

FIGURE 8.1 — The assessment process

assessment, this linear advancement is not entirely necessary. It is possible for parallel progress within an assessment process (e.g., existing documents are verified while waiting for the production of others) and between assessment processes (e.g., analysis of the DQOs for data quality assessment while data validation is being completed). *Typically, the focus of verification and validation is on the analytical process and on a data point by data point review, while data quality assessment considers the entire data collection process and the entire data set as it assesses data quality.*

Analytical data *verification* assures laboratory conditions and operations were compliant with the SOW based on project plan documents. The updated project plan documents specify the analytical protocols the laboratory should use to produce data of acceptable quality and the content of the analytical data package (see Section 1.5, "The MARLAP Process"). Verification compares the analytical data package delivered by the laboratory to these requirements (compliance), and checks for consistency and comparability of the data throughout the data package, correctness of basic calculations, data for basic calculations, and completeness of the results to ensure all necessary documentation is available. For example, there may be a SOW specification that requires the laboratory to correct for spectral interferences for a certain method. Data verification would confirm that a spectral interference correction factor was applied to each sample analysis. However, the data validation process determines whether the appropriate or correct spectral interference correction factor was used for each sample analysis. Data verification can be accomplished through the use of a plan or a simple checklist. A verification plan or checklist may be developed from the requirements contained in the SOW, laboratory contract, or project planning documents. The plan or checklist may include verification of generic laboratory and specific analytical information (outputs or records) that should be reported in a data package generated by the laboratory. Compliance verification may include a review of laboratory staff signatures (written or electronic), data and report dates, case narrative reports, sample identifiers, radionuclides and matrices for analyses, methods employed for analyses, preservation of samples, reference/sampling and analysis dates, spectral data, chemical yields, detector-efficiency factors, decay and ingrowth factors, radiological holding times, analytical results, measurement uncertainties, minimum detectable concentrations, daily instrument and batch QC results, etc.

The verification process produces a report identifying which requirements are not met (i.e., exceptions qualified with an "E" to alert the validator; see Section 8.3.3). The verification report is used to confirm laboratory compliance with the SOW and to identify problems that should be investigated during data validation. Verification works iteratively and interactively with the generator (i.e., laboratory) to assure receipt of all necessary data in the correct format. Although the verification process identifies specific problems, the primary function should be to apply appropriate feedback to the laboratory resulting in corrective action improving the analytical services before the project is completed.

Validation addresses the reliability of the data. The validation process begins with a review of the verification report and laboratory data package to identify its areas of strength and weakness.

This process involves the application of qualifiers that reflect the impact of not meeting the MQOs and any other analytical process requirements. Validation then evaluates the data to determine the presence or absence of an analyte, and the uncertainty of the measurement process. During validation, the technical reliability and the degree of confidence in reported analytical data are considered. The data validator should be a scientist with radiochemistry experience.

Validation flags (i.e., qualifiers) are applied to data that do not meet the performance acceptance criteria established in the SOW and the project plan documents. The products of the validation process are validated data and a validation report stating which data are acceptable, which data are sufficiently inconsistent with the validation acceptance criteria in the expert opinion of the validator, and a summary of the QC sample performance. The appropriate data validation tests should be established during the project planning phase. The point of validation is to perform a systematic check on a set of data being used to meet the project MQOs and any other analytical process requirements. Documenting that such a check cannot be done is an appropriate and essential validation activity. (For example, applying numerical tests to data already determined to be unreliable is of no value.)

Data Quality Assessment is the last phase of the data collection process, and consists of a scientific and statistical evaluation of project-wide knowledge to assess the usability of data sets. To assess and document overall data quality and usability, the data quality assessor integrates the data validation report, field information, assessment reports, and historical project data, and compares the findings to the original project DQOs. The DQA process uses the combined findings of these multi-disciplinary assessments to determine data usability for the intended decisions, and to generate a report documenting that usability and the causes of any deficiencies. It may be useful for a validator to work with the assessor to assure the value of the validation process (e.g., appropriateness of rejection decision) and to make the process more efficient. DQA will be covered in Chapter 9.

8.3 Validation Plan

The validation plan should integrate the contributions and requirements of all stakeholders and present this information in a clear, concise format. To achieve this goal, validation planning should be part of initial planning (e.g., directed planning process) to assure that the data will be validated efficiently to determine its reliability and technical defensibility in an appropriate context and to an appropriate degree.

The validation plan is an integral part of the project plan documents (Chapter 4), and should be included as either a section within the plan or as a stand-alone document attached as an appendix. The validation plan should be approved by an authorized representative of the project, the validation group performing the validation, and any other stakeholder whose agreement is needed.

The information and documentation identified in the validation plans should be communicated to the laboratory as part of the SOW. Integration of validation plan specifications, contractual requirements, and validator instructions/contracts is essential to ensure data collection process efficiency. Implementation of the data validation plan ensures that proper laboratory procedures are followed and that data are reported in a format useful for validation and assessment. This also improves the cost-effectiveness of the data-collection process.

The data validation plan should contain the following information:

- A summary of the project's technical and quality objectives in terms of sample and analyte lists, required measurement uncertainty, and required detection limit and action level on a sample/analyte-specific basis. It should specify the scope of validation, e.g., whether all the raw data will be reviewed and in what detail (Section 8.3.1).

- The necessary validation criteria (derived from the MQOs) and performance objectives deemed appropriate for achieving project objectives (Section 8.3.2).

- Direction to the validator on what qualifiers are to be used and how final qualifiers are assigned (Section 8.3.3).

- Direction to the validator on the content of the validation report (Section 8.3.4).

8.3.1 Technical and Quality Objectives of the Project

The identity of key analytes and how the sample results drive project decisions should be specified in the validation plan. In addition, the plan should define the association of required quality control samples with project samples.

This section of the validation plan should specify the following:

- Quality control acceptance criteria;

- Level of measurement uncertainty considered unusually high and unacceptable (tests of unusual uncertainty and rejection); and

- Action level and MQOs for detection and quantification capability (e.g., required detection and quantification limit).

The *quality control acceptance criteria* serve two purposes: (1) to establish if the analytical process was in control; and (2) to determine if project requirements were met. If the analytical process is in control, the assumption was that the analysis was performing within established limits and indicates a reasonable match among matrix/analyte/method. Generally, this means that

routine data quality expectations are appropriate. The *tests of unusual* (i.e., analysis not in control) *uncertainty* should verify the data meet the statistical confidence limits for uncertainty associated with the planning process. During validation, the uncertainty associated with sampling cannot be estimated. The *tests of detection* determine the presence or absence of analytes.

8.3.2 Validation Tests

Validating data requires three specific decisions that will allow the validator to qualify the data. The project planning team should determine:

- Which QC samples should be employed and how do they relate to the samples?
- Which validation tests are appropriate?
- What validation limits should be used for the specific tests?

The answers to these questions are driven by the need to know whether the data meets the MQOs for the project, and the allocation of resources between planning and implementation (i.e., conservative review may be more costly than real or perceived value in the decision). This section of the validation plan should address the following:

- Specific validation tests to be used, and
- Statistical confidence intervals or fixed limit intervals applied to each of the validation tests and criteria based on the MQOs for the project (see Appendix C, *Measurement Quality Objectives For Method Uncertainty and Detection And Quantification Capability*).

8.3.3 Data Qualifiers

Data qualifiers are codes placed on an analytical result that alert data users to the validator's or verifier's concern about the result. This section of the validation plan should outline:

- The basis for rejection or qualification of data; and
- The qualification codes that will be assigned.

These issues are discussed in detail in Section 8.5, which provides guidance for assigning data qualifiers.

The verification process uses a qualifier ("E") to alert the validator to noncompliance, including missing documentation, contract compliance, etc. This qualifier may be removed or replaced during validation, based on the validator's interpretation of the effect of the noncompliance on the data's integrity.

E A notice to the validator that something was noncompliant.

The validation process uses the qualifiers listed below to identify data points that do not meet the project MQOs or other analytical process requirements listed in the SOW or appropriate project plan document. The assignment of the "J" and "R" qualifiers relies heavily on the judgement and expertise of the reviewer and therefore, these qualifiers should be assigned as appropriate at the end of data validation.

U A normal, not detected (< critical value) result.

Q A reported combined standard uncertainty, which exceeds the project's required method uncertainty.

J An unusually uncertain or estimated result.

R A rejected result: the problems (quantitative or qualitative) are so severe that the data can not be used.

The data validator should be aware that a data qualifier or a set of qualifiers does not apply to all similar data. The data validator should incorporate the project MQOs into the testing and qualifying decision-making process.

During the data validation process the data validator may use additional qualifiers based on QC sample results and acceptance criteria. These qualifiers may be summarized as "U," "J," "R," or "Q" in the final validation report. The final validation reports should also include a summary of QC sample performance for use by the data assessor.

S A result with a related spike result (laboratory control sample [LCS], matrix spike [MS] or matrix spike duplicate [MSD]) that is outside the control limit for recovery (%R); "S+" or "S-" used to indicate high or low recovery.

P A result with an associated replicate result that exceeds the control limit.

B A result with associated blank result, which is outside the control limit, "B+" or "B-"used to indicate high or low results.

8.3.4 Reporting and Documentation

The purpose of this section is to define the format and program needs for validation reports and supporting documentation. This section should include:

- Documentation and records that should be included in a validation report;
- Disposition requirements for records and documents from the project;
- Report format, i.e., a summary table with results, uncertainties and qualifiers; and
- Procedures for non-conformance reporting, which detail the means by which the laboratory communicates nonconformances against the validation plan. The procedures should include all instances where the analytical data requirements and validation requirements established by the planning process and validation plan, respectively, cannot be met due to sample matrix problems or unanticipated laboratory issues (loss of critical personnel or equipment).

Detailed information about the validation report is presented in Section 8.6.

8.4 Other Essential Elements for Data Validation

Effective data validation is dependent on:

- A SOW and project plan documents that clearly define the data needs and the data quality requirements (i.e., MQOs); and
- A data package that has been verified for completeness, consistency, compliance, and correctness.

8.4.1 Statement of Work

The analytical services procurement options should be considered during the planning process. The SOW should specify the QC requirements that will be evaluated by the validator (see Chapter 5, *Obtaining Laboratory Services*). The elements that should be specified include, but are not limited to:

- External performance evaluation (PE) participation and acceptance criteria;
- Replicate sample frequency and acceptance criteria;
- LCS and acceptance criteria;
- Blank requirements and acceptance criteria;
- MS and MSD samples and acceptance criteria;
- Uncertainty calculations; and
- Sample result equations and calculations including corrections for yield, percent moisture, efficiencies and blank, if applied.

Section 8.5.2 provides guidance on evaluating QC sample results based on the project's MQO for measurement uncertainty.

8.4.2 Verified Data Deliverables

Verification compares the sample receipt information and the sample report delivered by the laboratory against the SOW and produces a report that identifies those requirements that were not met (called exceptions). Verification can be accomplished using a plan or checklist, which doesn't necessarily need to be project-specific. Verification exceptions normally identify:

- Required steps not carried out by the laboratory (i.e., correction for yield, proper signatures);
- Method QC not conducted at the required frequency (i.e., blanks, duplicates); and
- Method QC not meeting pre-set acceptance criteria (i.e., noncompliant laboratory control sample analysis).

The verifier checks the data package (paper or electronic) for completeness, consistency, correctness, and compliance. Completeness means all required information is present. Consistency means values are the same when reported redundantly on different reports, or transcribed from one report to another. Correctness means the reported results are based on properly documented and correctly applied algorithms. Compliance means the data pass numerical QC tests based on parameters or limits derived from the MQOs specified in the SOW.

The verifier should provide, within the verification package, checklists for contract or SOW specifications, noted deficiencies related to contract compliance, noted discrepancies or obvious quality related problems, and pertinent external QC results. *The verification package notes the deficiencies, discrepancies, and quality-related problems that could not be resolved with the laboratory.* The validator should take this information into consideration during the data validation process.

8.5 Data Verification and Validation Process

In its most basic form, data validation focuses on the reliability of each data point. After each point is evaluated, summary conclusions concerning the validity of groups of data (sets) are drawn and finally, after the reliability of all data sets has been established, an overall conclusion about the quality and defensibility of a project's analytical database is reached (DQA).

The first step in establishing the reliability of an analytical measurement is to determine that the measurement analytical process used in making the measurement is in control. That is, the sample handling and analysis system is performing within an accepted operating range

(established by instrument manufacturer, method, contract specifications, or long-term historical laboratory performance). After it has been determined that the measurement analytical process is in control, it is necessary to demonstrate that the sample is responding as expected when introduced into the measurement system.

The measurement process includes devices such as detectors for measuring radioactive decay emissions and balances for determining the mass of materials. The measurement process also includes the software that takes the output from the measurement device and calculates the result as a quantity of target radionuclide (activity/mass or activity/volume). The measurement process performance normally is specified by the SOW and appropriate project plan documents, and monitored by routine laboratory quality control procedures. Laboratory performance against these requirements is determined by the verification process.

When a sample is analyzed, new sources of variability are encountered in addition to those associated with the measurement process. These sources include laboratory subsampling, sample preparation (e.g., digestion, leaching, etc.), and sample matrix effects, to list a few. These processes, taken together with the previously discussed measurement process, comprise the analytical process.

The performance of the analysis can be predicted based on previous experience with similar materials. Analysis performance is monitored by laboratory quality control procedures specified in the SOW and appropriate project plan documents. Since each sample matrix, analyte, and method set is unique, the evaluation of overall analysis performance and resulting data is the role of a knowledgeable validator.

Using the validation plan, which specifies QC samples, validation tests, and validation limits, validation occurs in four stages:

- Determine whether the sample handling and analysis system is in control (Section 8.5.1);
- Determine whether QC sample analyses meet specified MQOs (Section 8.5.2);
- Apply validation tests of detection and unusual uncertainty (Section 8.5.3); and
- Determine final data qualifiers and document the results (Section 8.5.4).

For some methods (e.g., gamma spectrometry), identification of the analyte is also a primary decision. The laboratory's ability to identify analytes reliably is best checked by auditors and verified by reviewing the instrument's energy-calibration file.

8.5.1 The Sample Handling and Analysis System

As described in earlier sections of this guidance, it is necessary to know the extent to which the data delivered for validation meet the requirements of the SOW and appropriate project plan documents. These documents normally specify the minimum acceptable performance of the

analytical process. These specifications are the basis of the tests of quality control (QC tests) that establish that the sample handling and analysis system is in control at the time the analyses were performed. It is also necessary to know that all reporting requirements are complete. Normally, this evaluation against the requirements is made during the data verification process. If the data do not conform to the requirements, notification should be provided in the verification report.

The review of the verification package (and data package) by the validator determines if sufficient information is provided to proceed with data validation. The outcome of the verification process is the designation of exceptions to the quality control tests. These exceptions should be flagged with a qualifier (re-evaluated by the validator), which is appended to a data or report requirement that does not meet specifications to alert the validator of potential problems. The validator should then determine if sufficient reliable data are available to proceed with validation. The validator should use the data requirements and criteria developed in the validation plan to determine if the quality control exceptions have an adverse impact on one or more of the data points being validated.

Rarely, if ever, should quality control exceptions result in the decision to reject a complete data set. Those types of situations should have been detected by the laboratory during the analytical process and the samples reanalyzed. The validator should not reject (assign an "R" code) single data points based on a single QC test exception. Normally, only numerous QC exceptions *and* failures in one or more of the tests of detection and uncertainty are sufficient reason to reject data. The validation report should fully explain the assignment of all qualifiers as previously discussed.

The following paragraphs discuss some of the more important evaluations that should be applied to the sample handling and analysis system. *Some of these items (e.g., calibration, verification of self-absorption curves, and efficiency) may be checked during an audit instead of during data verification and validation.* Limited guidance is provided on how the QC test may impact data quality and defensibility.

8.5.1.1 Sample Descriptors

Sample descriptors include sample identification number, analytical method, analyte, and matrix, among others.

Criteria. Each sample should have a unique identifier code that can be cross-referenced to a unique sample or an internally generated laboratory sample. This unique identifier and associated sample descriptors should be included in all analytical reports to properly document the sample and requested analysis (Chapters 10, *Field and Sampling Issues that Affect Laboratory Measurements*, and 11, *Sample Receipt, Inspection, and Tracking*).

The matrix and other characteristics of the sample that affect method selection and performance should be clearly identified. The method(s) used in sample preparation and analysis should be identified. If laboratory replicate analyses are reported for a sample, they should be distinguishable by a laboratory-assigned code.

Verification. Check that criteria related to the sample description (e.g., stated description of sample type) have been addressed and pertinent documentation is included in the analytical data package. If necessary documentation is missing, the data should be flagged with an "E" code.

Validation. Missing information will decrease the confidence in any result reported on a sample(s) and justify the assignment of a "J" code. Missing information may be inferred from other information in the data package. For example, if the sample matrix is not provided, it may be inferred from:

- The aliquant units are expressed in units of mass or volume;
- The sample preparation method is specific for soils;
- The final results are expressed in units of mass; and
- The sampling report describes sampling soil.

The majority of related information should support the decision that the exception does not decrease the confidence in the result. If the supporting information is incomplete or conflicting, the assignment of a "J" code to data points is warranted. If documentation is inadequate to support the reporting of a data point, the data point should be qualified with an "R" code.

8.5.1.2 Aliquant Size

Criteria. The aliquant or sample size used for analysis should be documented so that it can be checked when reviewing calculations, examining dilution factors or analyzing any data that requires aliquant as an input. It is also imperative that the appropriate unit (liter, kilogram, etc.) is assigned to the aliquant.

Verification. Check that criteria related to sample aliquanting (e.g., stated aliquant size) have been addressed, and pertinent documentation is included in the analytical data package. If aliquant size documentation is missing, the data should be flagged with an "E" code.

Validation. The missing information will increase the uncertainty on any result reported on a sample(s) and justify the assignment of a "J" code.

8.5.1.3 Dates of Sample Collection, Preparation, and Analysis

Criteria. The analytical data package should report date of sampling, preparation, and analysis. These data are used to calculate radiological holding times, some of which may be specified in the sampling and analysis plan.

There are few circumstances where radiological holding times are significant for radionuclides. The best approach to minimize the impact of holding time on analysis is to analyze the samples as quickly as possible. Holding times may be applied to samples that contain radionuclides with short half-lives. Holding times would apply to these radionuclides to prevent reporting of high measurement uncertainties and MDCs, and to detect the radionuclide, if present at low concentration, before it decays to undetectable levels.

Verification. Check that criteria related to sample radiological holding time (e.g., stated date of sample collection and analysis) have been addressed, and pertinent documentation is included in the analytical data package. If information on radiological holding time is missing, the data should be flagged with an "E" code.

If a holding time is specified in the project plan documents or validation plan, the reported values should be compared to this specification. If the holding time is exceeded, the affected criteria (holding time) should be flagged with an "E" code.

Validation. The data points impacted by the missed holding time should be flagged with a "J" code by the validator or the justification for discounting the holding time impact described in the narrative section of the validation report.

8.5.1.4 Preservation

Criteria. Appropriate preservation is dependent upon analyte and matrix and should be defined in sampling and analysis documentation. Generally, radiochemical samples are preserved to prevent precipitation, adsorption to container walls, etc. The criteria (required presence or absence) for this QC process should be provided in the sampling and analysis plan (Chapter 10).

Verification. Check that criteria related to sample preservation (e.g., stated preservation technique or verification thereof) have been addressed, and pertinent documentation is included in the analytical data package. If information on sample preparation is missing, the data should be flagged with an "E" code.

Validation. If exceptions to the preservation criteria are noted, the validator should decide if a "J" code should be assigned to data points because the improper preservation increased the overall uncertainty in the data. In some cases where improper preservation severely impacts data

quality or defensibility (e.g., the use of acid preservation in water samples being analyzed for ^{14}C), the validator should assign an "R" qualifier. The assessor may elect to use the data, but they have the responsibility of addressing the data quality and defensibility in the assessment report.

8.5.1.5 Tracking

Criteria. Each analytical result should be linked to the instrument or detector on which it was counted. The requirement for this linkage normally is found in the project plan documents. The analytical sequence log (or some other suitable record) should be available in the data package submitted by the laboratory.

Verification. Check to see that the criteria related to instrument or detector linkage are found in the analytical data package. If the data are not linked to a counting instrument or detector, the data should be flagged with an "E" code.

Validation. The validator may consider the absence of linking a sample to a detection system into their evaluation of data quality and usability. At most, this should result in increasing the uncertainty of the determination and possibly assigning a "J" code to the data. This would not occur normally unless one or more of the detectors used in analyzing the samples was shown to be unreliable. Then, the inability to link a reliable detector to a sample increases the uncertainty of the data point(s).

8.5.1.6 Traceability

Criteria. The traceability of standards and reference materials to be used during the analysis should be specified in the sampling and analysis plan.

Verification. Check that criteria related to traceability of reference materials and standards (completed source manufacturer and internal calibration certificates) have been addressed, and pertinent documentation is included in the analytical data package or has been verified during an audit. If documentation on the traceability of reference materials and standards is missing, the data should be flagged with an "E" code.

Validation. The validator may factor the absence of the traceability into their evaluation of data quality and usability. At most, this should result in increasing the uncertainty of the determination and the possible assignment of a "J" code to the data. This would not occur normally unless one or more of the standards used in analyzing the samples was shown to be unreliable. Then, the inability to trace a reliable standard to a sample increases the uncertainty of the data point(s).

8.5.1.7 QC Types and Linkages

Criteria. The type and quantity of QC samples should be identified and listed in the SOW and the results provided by the laboratory in a summary report. Replicates and matrix spike results should be linked to the original sample results. The approximate level of matrix spike concentrations should be specified in the SOW, but the actual levels should be reported by the laboratory. The QC analyses should be linked to the original sample.

Verification. Check that there is linkage of QC samples to project samples and pertinent documentation is included in the analytical data package. If linkage information is missing, the data should be flagged with an "E" code.

Validation. The validator should compare any QC sample exceptions to similar ones that precede and follow the nonconforming QC sample. If these are in control, the validator can discount the impact of the single QC sample exception on the data results (i.e., analytical blunder). If a trend of failing values is found, the validator should consider if they affected a group of data points to the extent that the level of uncertainty was increased. This may warrant the assignment of a "J" code to the data.

8.5.1.8 Chemical Separation (Yield)

Criteria. Yield assesses the effects of the sample matrix and the chemical separation steps on the analytical result and estimates the analyte loss throughout the total analytical process. Yield is typically measured gravimetrically (with a carrier) or radiometrically (with a radiotracer). All the components in the calculation of the yield should be identified in a defined sequence. These specifications are found in the project plan documents.

Criteria for acceptable chemical yields may be given in the project plan documents. The criteria should be based on historical data for the method and matrix. In that case, yield is determined on both quality control samples and actual samples.

The most important yield-related question is whether the yield has been determined accurately. Typically, a yield estimate that is much greater than 100 percent cannot be accurate, but an estimate may also be questionable if the yield is far outside its historical range. Extremely low yields may lead to large measurement uncertainties.

Verification. Check that criteria related to chemical yield (e.g., calculated gravimetric or radiotracer yield determinations) have been addressed, and pertinent documentation is included in the analytical data package. If information on chemical yield is missing, the data should be flagged with an "E" code.

Validation. The experimentally determined yield is used to normalize the observed sample results to 100 percent yield. Exceptions to the yield value outside the range specified in the project plan documents may result in the validator assigning a "J" qualifier to otherwise acceptable data.

8.5.1.9 Self-Absorption

Criteria. For some radiochemical analytical methods, the SOW may specify the generation of a self-absorption curve, which correlates mass of sample deposited in a known geometry to detector efficiency.

Verification. For certain radionuclides, check that criteria related to self absorption curves (e.g., verification or copies of curves (or point-source values) covering the required weight ranges, emission type and energy) have been addressed and pertinent documentation is included in the analytical data package or has been verified during an audit. If the documentation is missing, the data should be flagged with an "E" code.

Validation. If required self-absorption curves are missing, the validator may qualify affected data with a "J" qualifier to signify an increased level of uncertainty in the measurement because of the inability to correct the measured value for self-absorption.

8.5.1.10 Efficiency, Calibration Curves, and Instrument Background

Criteria. For some methods based on decay-emission counting, efficiency is reported as measured count rate divided by the disintegration rate. For several methods, these efficiency determinations will depend on the energy of the emitted particle. For example, in gamma-ray spectrometry, a curve is fitted (measured activity/absolute disintegration rate) as a function of the gamma-ray energy for which this ratio is determined. A method like alpha spectrometry employs tracer radionuclides to determine a sample-specific "effective" efficiency factor, which is a product of the chemical yield and the detector efficiency. The specific efficiency criterion required for the project may be specified in the SOW. The determination of detector efficiency is a detailed process that is best checked during an audit of the laboratory's capabilities and is usually not part of the verification and validation process. Instrument background count rate is determined for each detector for each region of interest and subtracted from the sample count rate.

Verification. Check that each efficiency determination, efficiency calibration curve, and instrument background called for in the project plan documents is included in the analytical data package, if required. In many cases, this means assessing whether the proper calibration or efficiency was applied for the sample analyzed. If the documentation is missing, the data should be flagged with an "E" code. Each background subtracted should be appropriate for the

radionuclide of interest. The proper use of crosstalk factors is one example of proper background subtraction.

Validation. If required factors are missing, the validator may select to qualify affected data with a "J" qualifier to signify an increased level of uncertainty in the measurement because of the inability to correct the measured value for efficiency.

8.5.1.11 Spectrometry Resolution

Criteria. The measured resolution of alpha and gamma-ray spectrometers, in terms of the full width of a peak at half maximum (FWHM), can be used to assess the adequacy of instrument setup, detector selectivity, and chemical separation technique that may affect the identification and quantification of the analyte. When sufficient peak definition (i.e., sufficient number of counts to provide an adequate Gaussian peak shape) has been reached for a sample, the resolution of the analyte peak should be evaluated to determine if proper peak identification and separation or deconvolution was made. Spectral information should be provided in the data packages to accomplish this evaluation.

Verification. There are no established acceptance criteria, but resolution data (e.g., FWHM) should be provided in the package or available during an audit.

Validation. If required calculations (multiplet analysis) are missing, the validator may elect to qualify affected data with a "J" code to signify an increased level of uncertainty in the measurement. In addition, if severe peak interference has not been corrected properly, the data should be qualified with a "J" code. An "R" code may be applied if there is no separation of the analyte peaks.

8.5.1.12 Dilution and Correction Factors

Criteria. Samples for radiochemistry are usually not diluted, but a larger sample may be digested, taking an aliquant for analysis to obtain a more representative subsample. The dilution factors are normally used for tracers and carriers. Dilutions of the stock standards are prepared and added to the samples. This dilution normally affects yield calculations, laboratory control samples, and matrix spikes. This data should be provided in the data package so that the final calculations of all data affected by dilution factors can be recalculated and confirmed, if required.

Other correction factors that may be applied to the data are dry weight correction, ashed weight correction, and correction for a two-phased sample analyzed as separate phases.

Verification. Check that criteria related to sample dilution and correction factors (e.g., factors have been stated) have been addressed and pertinent documentation is included in the analytical

data package. If sample dilution information is missing, the data should be flagged with an "E" code.

Validation. Those results impacted by missing dilution factors should be flagged with a "J" or "R" qualifier, reflecting increased uncertainty in the data point(s). "R" may be warranted if the calculation cannot be confirmed due to missing data.

8.5.1.13 Counts and Count Time (Duration)

Criteria. The count time for each sample, QC analysis, and instrument background should be recorded in the data package. The ability to detect radionuclides is directly related to the count time.

Verification. Check that criteria related to instrument counting times (e.g., stated data about test source and background counting times) have been addressed and pertinent documentation is included in the analytical data package. If instrument or detector counting times are missing, the data should be flagged with an "E" code.

Validation. The validator should estimate the impact of the actual count times on the ability to detect the target analyte and the impact on the uncertainty of the measurement. *If the MQOs are met, the sample should not be qualified for count time.* The qualifiers should be adjusted accordingly and the justification provided in the validation report.

8.5.1.14 Result of Measurement, Uncertainty, Minimum Detectable Concentration, and Units

Criteria. MARLAP recommends that the result of each measurement, its expanded measurement uncertainty, and the estimated sample- or analyte-specific MDC be reported for each sample in the appropriate units. These values, when compared with each other, provide information about programmatic problems with the calculations, interference of other substances, and bias. The report should state the coverage factor used if calculating expanded measurement uncertainties, and the Type I and Type II error probabilities used to calculate MDCs.

Verification. Check to see that all criteria relating to linkages among result, measurement uncertainties, MDC, and sample identification are found in the analytical data package. If any of the criteria or actual linkages are missing, they should be flagged with an "E" code.

Validation. The validator should assign data qualifiers to those data points for which they feel sufficient justification exists. Each qualifier should be discussed in the validation report.

8.5.2 Quality Control Samples

Historically, data validation has placed a strong emphasis on review of QC sample data (laboratory control samples, duplicates, etc). The assumption is that if the analytical process was in control and the QC samples responded properly, then the samples would respond properly. It is possible to have excellent performance on simple matrices (e.g., QC samples), but unacceptable performance on complex matrices reported in the same batch as the QC samples. Directly evaluating the sample performance is essential to determine measurement uncertainty and the likelihood of false positive and negative detection of the target analyte.

Method blanks and laboratory control samples relate to the analytical batch (a series of similar samples prepared and analyzed together as a group) quality control function. They are required by most analytical service contracts, sampling and analysis plans, and project plan documents. They serve a useful function as monitoring tools that track the continuing analytical process during extended analytical sequences. They are the most ideal samples analyzed as part of a project. Normally, their performance is compared to fixed limits derived from historical performance or additionally project specific limits derived from the MQOs.

Laboratory duplicates and matrix spikes are quality control samples that directly monitor sample system performance. The laboratory duplicates (two equal-sized samples of the material being analyzed, prepared, and analyzed separately as part of the same batch) measure the overall precision of the sample measurement process beginning with laboratory sub-sampling of the sample. Matrix spikes (a sample containing a known amount of target analyte added to the sample) provide a direct measure of how the target analyte responds when the sample is prepared and measured, thereby estimating a possible bias introduced by the sample matrix.

Other QC tests can be applied to determine how the analytical process performs during the analysis of samples. These are yield, detector efficiency, test-source self-absorption, resolution, and drift. They are the same QC tests that were applied to routine QC samples (blanks and laboratory control samples) in the previous discussion of the analytical process, but now are applied to samples. The difference lies in how performance is measured. Fixed limits based on historical performance or statistics are usually the basis for evaluating the results of routine QC samples.

The following paragraphs discuss how QC tests should be used to determine if the results for QC samples meet the project MQOs. Guidance is provided on how to relate QC sample *and* sample performance to determine sample data quality and defensibility. Direction is also given about how to assign data qualifiers to sample data based on the tests of quality control. Appendix C provides guidance on developing criteria for evaluating QC sample results. Specifically, Appendix C contains equations that allow for the determination of warning and control limits for QC sample results based on the project's MQO for measurement uncertainty.

8.5.2.1 Method Blank

The method blank (Section 18.4.1) is generated by carrying all reagents and added materials normally used to prepare a sample through the same preparation process. It establishes how much, if any, of the measured analyte is contributed by the reagents and equipment used in the preparation process. For an ideal system, there will be no detected concentration or activity.

Measured results are usually corrected for instrument background and may be corrected for reagent background. Therefore, it is possible to obtain final results that are less than zero.

Criteria. The requirement for a method blank is usually established in the SOW and appropriate plan documents. The objective is to establish the target analyte concentration or activity introduced by the sample preparation sequence. Method blanks are normally analyzed once per analytical batch.

Other types of blanks, such as field blanks and trip blanks, are used to evaluate aspects of the data collection effort and laboratory operations that are not directly related to the validation of environmental analytical data quality or technical defensibility. They can be important to the overall data assessment effort, but are beyond the scope of this guidance (Chapter 10).

See Appendix C (*Measurement Quality Objectives for Method Uncertainty and Detection and Quantification Capability*) for guidance on developing criteria for evaluating blanks based on the project's MQO for method uncertainty.

Verification. If a method blank was required but not performed, or if the required data are missing, the verifier flags the data with an "E" code.

Validation. If a blank result does not comply with the established criteria, the associated samples are flagged "B+" to indicate that the blank result is greater than the upper limit, or "B-" to indicate that the blank result is less than the lower limit.

8.5.2.2 Laboratory Control Samples

The laboratory control sample (LCS) is a QC sample of known composition or an artificial sample (created by spiking a clean material similar in chemical and physical properties to the sample), which is prepared and analyzed in the sample manner as the sample (see Section 18.4.3, "Laboratory Control Samples, Matrix Spikes, and Matrix Spike Duplicates"). In an ideal situation, the LCS would give 100 percent of the concentration or activity known to be present in the fortified sample or standard material. Acceptance criteria for the LCS sample are based on the complexity of the matrix and the historical capability of the laboratory and method to recover the activity. The result normally is expressed as percent recovery.

Criteria. The objective of the LCS is to measure the response of the analytical process to a QC sample with a matrix similar to the sample. This will allow inferences to be drawn about the reliability of the analytical process.

See Appendix C for guidance on developing control limits for LCS results based on the project's MQO for method uncertainty.

Verification. If a required LCS is not analyzed, or if required information is missing, the verifier flags the data with an "E" code.

Validation. When the measured result for the LCS is outside the control limits, the associated samples are flagged with the "S" qualifier (S+ or S-).

8.5.2.3 Laboratory Replicates

Replicates are used to determine the precision of laboratory preparation and analytical procedures. Laboratory replicates are two aliquants selected from the laboratory sample and carried through preparation and analysis as part of the same batch.

The discussion of field replicates is beyond the scope of this chapter.

Criteria. The objective of replicate analyses is to measure laboratory precision based on each sample matrix. The variability of the samples due to the analyte's heterogeneity in the sample is also reflected in the replicate result. The laboratory may not be in control of the precision. Therefore, replicate results are used to evaluate reproducibility of the complete laboratory process that includes subsampling, preparation, and analytical process.

See Appendix C for guidance on developing control limits for replicate results based on the project's MQO for method uncertainty.

Verification. If replicate analyses are required but not performed, or if the required data are not present in the report, the verifier flags the data with an "E" code.

Validation. When the replicate analysis is outside the control limit, the associated samples are flagged with the "P" qualifier.

8.5.2.4 Matrix Spikes and Matrix Spike Duplicates

A matrix spike is typically an aliquant of a sample fortified (spiked) with known quantities of target radionuclides and subjected to the entire analytical procedure to establish if the method or procedure is appropriate for the analysis of a particular matrix. In some cases, specifically

prepared samples of characterized materials that contain or are spiked with the target radionuclide and are consistent with the sample matrix may be used as matrix spikes. Matrix spike duplicates are used in a similar fashion as laboratory sample replicates, but in cases where there are insufficient quantities of target radionuclides in the laboratory sample replicates to provide statistically meaningful results.

Criteria. Matrix spike samples provide information about the effect of each sample matrix on the preparation and measurement methodology. The test uncovers the possible existence of recovery problems, based on either a statistical test or a specified fixed control limit.

See Appendix C for guidance on developing criteria for evaluating matrix spikes based on the project's MQO for method uncertainty.

Verification. If a required matrix spike analysis was not performed, or if the required information is missing, the data should be flagged with an "E" code.

Validation. If the results of the matrix spike analysis do not meet the established criteria, the samples should be qualified with an "S+" or "S-" indicating unacceptable spike recoveries.

8.5.3 Tests of Detection and Unusual Uncertainty

8.5.3.1 Detection

The purpose of a test of detection is to decide if each result for a regular sample is significantly different from zero. Since most radiochemistry methods always produce a result, even if a very uncertain or negative one, some notion of a non-detected but measured result may be needed for some projects. A nondetected result is generally as valid as any other measured result, but it is too small relative to its measurement uncertainty to give high confidence that a positive amount of analyte was actually present in the sample. Ordinarily, if the material being analyzed is actually analyte-free, most results should be "nondetected."

For some projects, detection may not be an important issue. For example, it may be known that all the samples contain a particular analyte, and the only question to be answered is whether the mean concentration is less than an action level. However, all laboratories should be able to perform a test of detection routinely for each analyte in each sample.

Criteria. An analyte is considered detected when the measured analyte concentration exceeds the critical value (see Chapter 20, *Detection and Quantification Capabilities*). Both values are calculated by the laboratory performing the measurement; so, the detection decision can be made at the laboratory and indicated in its report. If there is no evidence of additional unquantified

uncertainty in the result (e.g., lack of statistical control or blank contamination), the laboratory's decision may be taken to be final.

Verification. Typically, the role of the verifier is limited to checking that required information, such as the critical value, is present in the report. If information is missing, the result should be flagged with an "E" code.

Validation. The validator examines the result of the measurement, its critical value, and other information associated with the sample and the batch in which it was analyzed, including method blank results in particular, to make a final determination of whether the analyte has been detected with confidence. If the data indicates the analyte has been detected in both the sample and the method blank, its presence in the sample may be questionable. A quantitative comparison of the total amounts of analyte in the sample and method blank, which takes into account the associated measurement uncertainties, may be needed to resolve the question.

8.5.3.2 Detection Capability

Criteria. If the project requires a certain detection capability, the requirement should be expressed as a required minimum detectable concentration (RMDC). The data report should indicate the RMDC and the sample-specific estimate of the actual minimum detectable concentration (MDC) for each analyte in each sample.

In some situations, it may not be necessary or even possible for a laboratory to meet the MDC requirement for all analytes in all samples. In particular, if the analyte is present and quantifiable at a concentration much greater than the action level, a failure to meet a contract-required detection limit is usually not a cause for concern. A failure to meet the RMDC is more often an important issue when the analyte is not detected.

Verification. The RMDC specified in the contract is compared to the sample-specific MDC achieved by the method. The analytes that do not meet the RMDC are flagged with an "E" code.

Validation. If the sample-specific MDC estimate exceeds the RMDC, the data user may be unable to make a decision about the sample with the required degree of certainty. A "UJ" qualifier is warranted if the estimated MDC exceeds the RMDC and the analyte was not detected by the analysis. A final decision about the usability of the data should be made during the data assessment phase of the data collection process.

An assignment of "R" to the data points affected by this type of exception may be appropriate in some cases, but the narrative report may classify the data as acceptable (no qualifier), "U," or "J," based on the results of the tests of detection and uncertainty. This allows the assessor to make an

informed judgement about the usability of the data point(s) and allows them the opportunity to provide a rationale of why the data can be used in the decision process.

8.5.3.3 Large or Unusual Uncertainty

When project planners follow MARLAP's recommendations for developing MQOs, they determine a required method uncertainty at a specified analyte concentration. The required method uncertainty is normally expressed in concentration units, but it may be expressed as a relative method uncertainty (percent based on the upper bound of the gray region, which is normally the action level). It is reasonable to expect the laboratory's combined standard uncertainty at concentrations lower than the action level to be no greater than the required method uncertainty (expressed in concentration units) and to expect the laboratory's relative combined standard uncertainty at concentrations above the action level to be no greater than the required relative method uncertainty (expressed as a percent). Each measured result should be checked against these expectations (see Appendix C).

Criteria. The reported combined standard uncertainty is compared to the maximum allowable standard uncertainty. Either absolute (in concentration units) or relative uncertainties (expressed as a percent) are used in the comparison, depending on the reported concentration. The result is qualified with a "Q" if the reported uncertainty is larger than the requirement allows.

Verification. The test for large uncertainty is straightforward enough to be performed during either verification or validation. If there is a contractual requirement for measurement uncertainty, the verifier should perform the test and assign the "E" qualifier to results that do not meet the requirement. Note that it may sometimes happen that circumstances beyond the control of the laboratory make it impossible to meet the requirement.

Validation. If a "Q" qualifier is assigned, the validator may consider any special circumstances that tend to explain it, such as interferences, small sample sizes, or long decay times, which were beyond the control of the laboratory. He or she may choose to remove the qualifier, particularly if it is apparent that the original uncertainty requirement was too restrictive.

8.5.4 Final Qualification and Reporting

The final step of the validation process is to assign and report final qualifiers for all regular sample results. The basis for assignment of final qualifiers is qualifiers and reasons from all previous tests, patterns of problems in batches of samples, and validator judgement.

The difficult issue during final qualifier assignment is rejecting data. What follows summarizes some of the issues to consider when thinking about rejecting data.

Rejecting a result is an unconditional statement that it is not useable for the intended purpose. A result should only be rejected when the risks of using it are significant relative to the benefits of using whatever information it carries. If the DQA team or users feel data is being rejected for reasons that don't affect usability, they may disregard all validation conclusions. Rejected results should be discarded and not used in the DQA phase of the data life cycle.

There are three bases on which to reject data:

1. Insufficient or only incorrect data are available to make fundamental decisions about data quality. For example, if correctly computed uncertainty estimates are not available, it is not possible to do most of the suggested tests. If the intended use depends on a consistent, high level of validation, it may be proper to reject such data.

   The missing data should be fundamental. For example, missing certificates for standards are unlikely to be fundamental if laboratory performance on spiked samples is acceptable. In contrast, if no spiked sample data is available, it may be impossible to determine if a method gives even roughly correct results, and rejection may be appropriate.

2. Available data indicate that the assumptions underlying the method are not true. For example, QC samples may demonstrate that the laboratory's processes are out of control. Method performance data may indicate that the method simply does not work for particular samples. These problems should be so severe that is not possible to make quantitative estimates of their effects.

3. A result is "very unusually uncertain." It is difficult to say what degree of uncertainty makes a result unusable. Whenever possible, uncertain data should be rejected based on multiple problems with one result, patterns in related data, and the validator's judgement, not the outcome of a single test. This requires radiochemistry expertise and knowledge of the intended use.

Based on an evaluation of the tentative qualifiers, final qualifiers are assigned to each regular sample result.

After all necessary validation tests have been completed and a series of qualifiers assigned to each data point based on the results of the tests, a final judgment to determine which, if any, final qualifiers will be attached to the data should be made. The individual sample data from the laboratory should retain all the qualifiers. The basic decision making process for each result is always subject to validator judgement:

- As appropriate, assign a final "R";

- If "S", "P", or "B" were assigned, determine whether the qualifiers warrant the assignment of an "R";

- If "R" is not assigned, but some test assigned a tentative S, P, B, Q, or J, or a pattern exists that makes it appropriate, assign a final S, P, B, Q, or J and summarize QC sample performance;

- If a final S, B, or J was assigned, + or -, but not both, was tentatively assigned, and the potential bias is not outweighed by other sources of uncertainty, make the + or - final; and

- For non-R results, if any test assigned a tentative "U," make it final.

The final validation decision should address the fact that the broader purpose of validation is to contribute to the total data collection process, i.e., effectively translate and interpret analytical results for efficient use by an assessor. This means the validator should examine the full range of data available to search for and utilize relationships among the data elements to support the acceptance and use of data that falls outside method or contract specifications and data validation plan guidance.

8.6 Validation Report

The final product of validation is a package that summaries the validation process and its conclusions in an orderly fashion. This package should include:

- *A narrative or summary table written by the validator that summarizes exceptional circumstances*: In particular, it should document anything that prevented executing the planned validation tests. Further, the narrative should include an explicit statement explaining why data has been rejected or qualified based on the findings of the validation tests and the validator's judgment.

- *A list of validated samples that provides a cross-reference of laboratory and client sample identifiers*: This report should also include other identifiers useful in the context of the project, such as reporting batch, chain of custody, or other sample management system sample information.

- *A summary of all validated results with associated uncertainty for each regular sample with final qualifiers*: Unless specified in the sampling and analysis plan, non-detects are reported as measured, not replaced by a detection limit or other "less than" value.

- A summary of QC sample performance and the potential effect on the data both qualified and not qualified.

Assuming the client wants additional information, the following, more detailed reports can be included in the validation package. Otherwise, they are simply part of the validation process and the verification contract compliance:

- A detailed report of all tentative qualifiers and associated reasons for their assignment;
- QC sample reports that document analytical process problems; and
- Reports that summarize performance by method—these should support looking across related analyses at values such as yields and result ratios.

The data in the summary reports should be available in a computer-readable format. If no result was obtained for a particular analyte, the result field should be left blank. The validation report should package analytical results as effectively as possible for application and use by the individual assembling and assessing all project data.

The validation report should contain a discussion describing the problem(s) found during the validation process. For the validation codes, the discussion summarizes the performance criteria established in the validation plan. If the validation test performance criteria were changed (e.g., increased or decreased level of unusual uncertainty) because the nature of the sample matrix or analyte was different than expected, the new criteria should be explained in the report and the qualifiers applied using the new criteria. The approval of the project manager should be obtained (and documented) before the new criteria are applied. The project manager should communicate the changes to the project planning team to maintain the consensus reached and documented during validation planning.

Well-planned and executed analytical activities can be expected to meet reasonable expectations for data reliability. This means that for most data points or data sets, the results of the tests of quality control, detection, and unusual uncertainty will show that the data are of sufficient quality and defensibility to be forwarded to the assessor with little or no qualification for final assessment. A small number of points will be rejected because random errors in the analytical process or unanticipated matrix problems resulted in massive failure of several key validation tests.

A smaller number of data points will show conflicting results from the validation tests and present the greatest challenge to the validator. The more important the decision and the lower the required detection limit, the more common this conflict will become, and the more critical it is that the data validation plan provide guidance to the validator about how to balance the conflicting results. Is the ability to detect the analyte more important than the associated statistical unusual uncertainty, or is the presence of the analyte relatively definite but the unusual uncertainty around the project decision point critical to major decisions? The necessary guidance should be developed during the planning phase to guide the final judgment of the validator.

8.7 Summary of Recommendations

- MARLAP recommends that project objectives, implementation activities and QA/QC data be well documented in project plans, reports, and records, since the success of the assessment phase is highly dependent upon the availability of such information.

- MARLAP recommends that calibration be addressed in a quality system and through an audit, although demonstration of calibration may be required as part of a project's deliverables.

- MARLAP recommends that the assessment criteria of a project be established during the directed planning process and documented in the respective plans as part of the project plan documents.

- MARLAP recommends that the result of each measurement, its expanded measurement uncertainty, and the estimated sample- or analyte-specific MDC be reported for each sample in the appropriate units.

8.8 Bibliography

American National Standards Institute (ANSI) N13.30. *Performance Criteria for Radiobioassay*. 1996.

U.S. Environmental Protection Agency (EPA). 1994. *Contract Laboratory Program National Functional Guidelines for Inorganic Data Review*. EPA-540/R-94-013 (PB94-963502). February. Available from www.epa.gov/oerrpage/superfund/programs/clp/download/fginorg.pdf.

U.S. Environmental Protection Agency (EPA). 2002. *Guidance on Environmental Data Verification and Data Validation* (EPA QA/G-8). EPA/240/R-02/004. Office of Environmental Information, Washington, DC. Available at www.epa.gov/quality/qa_docs.html.