7 EVALUATING METHODS AND LABORATORIES

7.1 Introduction

This chapter provides guidance for the initial and ongoing evaluation of radioanalytical laboratories and methods proposed by laboratories. Appendix E, *Contracting Laboratory Services*, provides additional guidance on the initial laboratory evaluation. More details about evaluating and overseeing a laboratory's performance can be found in ASTM E1691 and ASTM E548.

The performance-based approach to method selection allows a laboratory the freedom to propose one or several methods for a specific analyte/matrix combination that will meet the needs of the analytical protocol specifications (APSs) and measurement quality objectives (MQOs) delineated in the statement of work (SOW). However, the laboratory should demonstrate, through a method validation process, that the method is capable of producing analytical results of quality that meet the needs of the SOW (Chapter 5, *Obtaining Laboratory Services*). Guidance and recommendations on the selection of an analytical method based on the performance-based approach is presented in Chapter 6 (*Selection and Application of an Analytical Method*). Section 7.2 provides guidance on how to evaluate the methods proposed by a laboratory. Section 7.3 provides guidance on the initial evaluation of a laboratory, and Section 7.4 discusses the continual evaluation of the quantitative measures of quality and operational aspects of the laboratory once sample processing has commenced.

Method applicability and performance compliance should be demonstrated prior to the initiation of the sample analyses, as well as during the project period. A defined logical process for demonstrating and documenting that the analytical method selected meets the project's data needs and requirements may involve, for example, a review of the method validation documentation, an evaluation of past performance data from other projects (if available), the analysis of external performance evaluation (PE) program results, the analysis of matrix-specific standard reference materials (or method validation reference materials) sent during the initial work period and throughout the project, and the final evaluation of the performance during the data verification and validation process (see Chapter 8, *Radiochemical Data Verification and Validation*).

In addition to the evaluation of the analytical methods, the capability of the laboratory to meet all SOW requirements needs to be reviewed and evaluated. Supporting information, such as method validation documentation, safety manuals, licenses and certificates, and quality manual are typically submitted with the response to the request for proposals (RFP). A generic evaluation of the laboratory operation may be conducted during the initial laboratory audit or assessment. This may be an initial

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onsite audit. This first evaluation covers those generic SOW requirements dealing with the laboratory's capability and operation, including verification of adequate facilities, instrumentation, and staffing and staff training and qualifications. Following the first audit, emphasis should be on ensuring the laboratory continues to meet the APSs through a continuous or ongoing evaluation effort.

7.2 Evaluation of Proposed Analytical Methods

A laboratory may submit several methods for a particular APS contained in the SOW, but each method should be evaluated separately and, if appropriate, approved by the project manager or designee. The method should be evaluated to be consistent with the overall analytical process that includes the proposed field sampling and preservation protocols (Chapter 1). The project manager may delegate the method review process to a technical evaluation committee (TEC) that has a radioanalytical specialist. MARLAP recommends that a radioanalytical specialist review the methods for technical adequacy. The acceptance, especially of a new method, may be the most critical aspect of the performance-based approach for method selection. Acceptance of the method requires the project manager to verify that the method is scientifically sound.

Each step of the method should be evaluated by a radioanalytical specialist in order to understand how the results are derived. These steps may involve sample digestion, analyte purification and decontamination steps that use ion exchange, solvent extraction, precipitation or oxidation/ reduction applications. Once these steps have been reviewed, and the method evaluation data (e.g., from method validation documentation or various performance evaluation results) confirm that the proposed method is acceptable, the project manager should have the confidence necessary to endorse and verify the use of the method in the analysis of the routine samples.

As discussed in Chapter 6, the laboratory should provide method validation and analytical data that demonstrates method performance. The data should show conclusively that the proposed method meets the requirements as defined by the APSs. If method performance is questionable, additional data may be required. For such cases, the project manager may decide to send performance testing (PT) materials to the laboratory in order to evaluate or validate the method. The preparation of the PT material used to evaluate the method should be based on sound scientific principles and representative of the expected sample matrix (see Chapter 6 on method validation options using site-specific materials). If there is sufficient reason to believe that the PT material is an adequate substitute for the sample matrix and that the laboratory will follow the same method, then the need to justify each step in the method may be drastically reduced.

7.2.1 Documentation of Required Method Performance

Certain documentation submitted by the laboratory with the proposed methods, as well as available external information on the laboratory's analytical performance, should be reviewed

and evaluated by the radioanalytical specialist. Table 7.1 outlines where such information typically can be found by the TEC. This section will discuss various information categories that may be available during the method evaluation process.

TABLE 7.1 — Cross reference of information available for method evaluation

Evaluation Element Addressed	Method Validation	Internal and External QC Reports	External PE Programs	Internal/ External QA Assessments	Information from RFP and Other Sources
Analyte/Matrix	●				●
Process Knowledge					●
Previous Experience					●
Radiological Holding Time	●	○	○	●	●
Turnaround Time		○	○	●	●
Unique Process Specifications	●				●
Bias	●	●	●	○	●
Method Uncertainty (MQC/MDC)	●	●	●	○	●
Analyte/Interference Range	●	●	●		●
Method Ruggedness	●	○	●	●	●
Method Specificity	●	○	●	●	●

● Information relevant to method evaluation should be present.
○ Information relevant to method evaluation may be present.

7.2.1.1 Method Validation Documentation

Chapter 6 outlines the various method validation options that can be specified by the project manager. In the MARLAP process, the method validation requirements will be contained in the SOW. The laboratory must submit the necessary method validation documentation consistent with the SOW specification. The laboratory may choose to validate a method to a higher degree of validation or to submit method validation documentation for a higher degree of validation than that specified by the SOW. The radioanalytical specialist or project manager should review the documentation to ensure that validation criteria for the number of analyte concentration levels and replicates meet or exceed the required validation criteria (Chapter 6, Table 6.1). Although not specified in the method validation protocol, some laboratories may include chemical and analytical interferences in their method validation plan to gain a perspective on the method's specificity and ruggedness. However, it should be noted that the graded approach to method validation presented in Chapter 6 does inherently increase the degree of ruggedness in terms of

having the method address site-specific materials which may include chemical and radionuclide interferences.

In addition to reviewing the documentation for compliance with the method validation protocol, the results of the method validation process should be evaluated to determine if the project specific MQOs will be met. The method validation may or may not have been specifically conducted for the project at hand. When the method has been validated (Chapter 6, Section 6.6) to the SOW specifications (validation level and MQOs), then evaluation of the documentation can be straight forward. If the method has been previously validated for the MQOs of other projects, then the laboratory should provide a justification and calculations to show that the method validation results will meet the MQOs for the new project. The TEC should verify these calculations and review the assumptions and justifications for reasonableness and technical correctness.

7.2.1.2 Internal Quality Control or External PE Program Reports

The documentation of internal QC and external PE program results should be reviewed relative to the MQOs. Method uncertainty and internal biases can be estimated from the information available in the laboratory's internal quality control reports, summaries of batch QC results that may be submitted with the RFP response and external PE program reports. The TEC should review these documents and, when possible, estimate the method uncertainty and bias for various analyte concentration levels. However, it is imperative that no confusion exists in terms of what method produced the results: the proposed method or another method available to the laboratory. This is especially important when reviewing external PE program results. It should also be noted that although a laboratory may meet performance acceptance criteria for an external PE program, this fact may have no bearing on whether the method will meet the MQOs of the SOW.

Review of the internal batch QC data can provide additional information on typical sample analysis times and rates of blank contamination and sample reanalysis. This information is important when comparing methods (from the same or between laboratories) in terms of APS characteristics. The frequency of blank contamination would be very important to national characterization studies (groundwater or soil analyses) for the determination of ambient analyte levels. Method evaluation for these projects may weight the blank contamination rate more heavily than other SOW parameters. The rate of sample reanalysis would be important to projects having pending operations that are conducted based on a short sample processing turnaround time (TAT). In some site remediation projects, the contractor may remain onsite pending analytical results. A delay in reporting data or not meeting a TAT due to sample reanalysis may be costly. Projects of this nature may weight TAT and low sample reanalyses more heavily than other SOW parameters.

7.2.1.3 Method Experience, Previous Projects, and Clients

When permitted by former clients, the laboratory may submit information relative to the previous or ongoing clients and projects for which the proposed method has been used. The TEC should verify with the laboratory's clients that the laboratory has previous experience using the method. When available and allowed, the information should also include the analyte(s) and interferences and their applicable concentration range, matrix type, and project size in terms of the number of samples per week or other time periods. From this information, the TEC can evaluate whether or not to contact the laboratory's client for further information on the operational adequacy of the method. The client may offer some information on the quality of the results based on their external single- or double-blind QC program, percent completion of reports, TAT, and sample re-analysis frequency. The sharing of laboratory assessment reports may be advantageous when reviewing the performance of the laboratory during its employment of the method.

7.2.1.4 Internal and External Quality Assurance Assessments

When available, internal and external quality assurance assessment reports should be evaluated to determine the adequacy of the method performance based on previous projects. Problems with the conduct of the method due to procedural and technical issues may be readily evident. These issues may include an ineffective corrective action program creating delayed remedies to problems, insufficient understanding of the method, inadequate training of staff, internal and project-specific QC issues, and higher-than-expected failure rates for sample TATs and re-analyses. Information in these reports may disclose problems with a particular method that are not common to another proposed method. As such, the TEC may give one method a higher weighting factor than another method.

7.2.2 Performance Requirements of the SOW—Analytical Protocol Specifications

Under the performance-based approach to method selection, a laboratory will propose one or several analytical methods that can meet the stated APSs and MQOs in the SOW for a given analyte and matrix combination. Chapters 3, 5, and 6 discuss the APSs and MQOs in detail in terms of their basic description, their inclusion in a SOW, and as key considerations for identifying existing validated methods or developing new methods. The purpose of this section is to provide guidance on what available information should be evaluated in order to approve the various proposed methods.

The radioanalytical specialist should review the process-knowledge information and determine if the proposed method is adequately specific, rugged, and applicable to address these issues. Discussions on method specificity and ruggedness may be found on in subsections on pages 7-12 and 7-13, respectively.

As discussed in Section 6.5.2 and above, process knowledge is extremely important for identifying potential radioanalytical problems on some projects. Historical information or process knowledge may identify chemical and radionuclide interferences, expected analyte and interfering radionuclide concentration ranges, sample analyte heterogeneity issues, and the physiochemical form of the analyte, and the sample matrix substrate. In some special cases, it may be necessary to determine if the radiological holding time will be an issue if the laboratory must analyze an alternative nuclide to determine supported and unsupported radionuclides (decay progeny nuclides) in the matrix.

The following subsections cover key aspects of the SOW that should be addressed during the method evaluation and approval process.

7.2.2.1 Matrix and Analyte Identification

The TEC should review the method(s) proposed by the laboratory to determine if the method under evaluation is applicable for the analyte/matrix combination specified in the SOW. In some cases, several methods may be proposed, including gross screening methods and specific radionuclide or isotopic methods having high specificity and ruggedness (Section 6.5.1.1 has additional guidance). Each method should be evaluated on its own application and merit. When methods are proposed by the laboratory that use alternative nuclides (such as decay products) to determine the analyte of interest, the TEC should carefully review the objective or summary of the method to determine if the proposed method is truly applicable for the analyte of interest given the radiological holding time and MQOs (i.e., can it properly quantify the analyte of interest through decay progeny measurements?). For gross screening techniques, the TEC should evaluate the analyte's decay scheme to determine the underlying gross radiation category (beta, alpha, X-ray, or gamma-ray emitting) and the applicability of the proposed method's radiation detection methodology.

Each proposed method should be evaluated to determine if the method can analyze the sample matrix identified in the SOW. A method validated for water cannot be applied to soil samples without modification and validation (Section 6.5). The planning team should have made—through historical process knowledge, previous matrix characterization studies or common experience—a determination on the uniqueness of the site-specific matrices compared to typical matrices and provided guidance in the SOW as to the level of method validation. In addition, if the radioanalytical specialist of the project planing team is concerned that the physiochemical form of the analyte or the sample matrix substrate may present special problems to the radioanalytical process, a detailed description of the analyte and matrix should have been included in the SOW. Chapters 12 (*Laboratory Sample Preparation*) and 13 (*Sample Dissolution*) discuss possible sample matrix problems and Section 6.5 provides guidance on the need for method validation. The radioanalytical specialist should carefully review the summary of the method to determine if the proposed method is applicable for the sample matrix.

At this point, if it is determined that the proposed method(s) is not applicable and cannot meet the SOW specifications, there is no need to continue the method evaluation process.

7.2.2.2 Radiological Holding and Turnaround Times

The radioanalytical specialist also should review the proposed method in light of the radiological holding time, analyte's half-life and typical sample delivery options and determine if the method is capable of meeting the MQOs in a reasonable counting period given the typical method parameters (such as sample weight processed, chemical yields, radiation detection efficiency, branching ratio and background, ingrowth periods for decay progeny analysis, etc.). Radiological holding time is defined as the time between the sample collection and the end of the sample-counting interval, while sample processing TAT refers to the time between sample receipt at the laboratory and the issuance of an analytical report. The physical (analyte's half-life) and chemical (stability or preservation concerns) characteristics of the analyte, as well as biological degradation for some matrices, usually will dictate the radiological holding time. Project-specific schedules and practicalities related to project and laboratory processing capacities normally enter into establishing TATs. If the radiological holding time appears to be a critical issue, then the client should request information on the typical batch size being processed by the laboratory for that method. This information is needed in the method evaluation and review process. For very short-lived analytes, too large a batch size may result in the later samples having much larger uncertainties than the earlier samples. In these cases, the laboratory will count the sample (or final processing products) longer in order to achieve client-requested minimum detectable concentrations. This is not often practical because the loss of counts due to analyte decay is more significant than any gain achieved by counting the sample longer.

In some cases, the laboratory may want to propose two methods for a short-lived analyte: one for normal delivery and processing schedules and another method for situations when lower detection limits are needed. An example of such a situation is the analysis of ^{131}I in environmental media. A method with adequate detection limits for reasonable radiological holding times is gamma spectrometry. Another method that can be applied for lower detection limits or longer radiological holding times is radiochemical separation followed by beta-gamma coincidence counting.

Certain projects may be concerned with the chemical speciation of the analyte in the sample. For these projects, the radiological holding time should have been specified to ensure that the chemical species are not altered prior to processing. The project normally should specify chemical preservation specifications applicable at the time of sample collection.

Preservation techniques should be used when deterioration of biological samples may become a problem (Chapter 10, *Field and Sampling Issues that Affect Laboratory Measurements*). However, the radiological holding time should be specified to limit problems with sample degrada-

tion. The radioanalytical specialist should evaluate the method in light of the foregoing information and determine its adequacy to meet the radiological holding time and the pertinent MQOs

A laboratory's sample (processing) TAT for a method typically is not related to the method's technical basis unless the radiological holding time and the TAT are nearly equal for a short-lived analyte. However, sufficient time should be available between the completion of sample analysis and the delivery of the analytical report. Meeting the radiological holding time but failure to meet the TAT will not affect the quality of the analytical results but may place a hardship on the project to meet schedules. The TEC should review the proposed method, the radiological holding time and the TAT to determine if the method can process the samples in a reasonable time period to meet the TAT. The sample delivery rate, sample batch size, level of data automation and the laboratory's existing sample processing capacity will affect the laboratory's ability to meet the TAT requirement.

7.2.2.3 Unique Processing Specifications

The TEC should review the proposed methods for compliance or applicability to unique sample processing specifications stated in the SOW. Chapter 6 provides a limited discussion on what a project may identify as unique or special sample process specifications. Examples may include chemical speciation, analyte depth profiles, analyte particle size distribution, analyte heterogeneity within the sample, wet-to-dry analyte concentration ratios in biologicals, and possible scaling factors between radionuclides in the sample. In some cases, the proposed method(s) for the analyte(s) may have to be evaluated with respect to all analytes or other sample preparation specifications in order to determine method applicability and adequacy.

7.2.2.4 Measurement Quality Objectives

Method performance characteristics (method uncertainty, quantification capability, detection capability, applicable analyte concentration range, method specificity, and method ruggedness) will be discussed in the following subsections. For a particular project, MQOs normally will be developed for several (but not all) of the performance characteristics discussed below.

METHOD UNCERTAINTY

The SOW should specify the required method uncertainty at a stated analyte concentration (or activity level) for each sample matrix and the level of method validation (Section 6.6) needed to qualify the method at the stated analyte concentration.

MARLAP uses the term "method uncertainty" to refer to the predicted uncertainty of a result that would be measured if a method were applied to a hypothetical laboratory sample with a specified analyte concentration. As presented in Chapter 6 and formulated in Chapter 20 (*Detection and Quantification Capabilities*), the method uncertainty of the analyte concentration for a given

method is determined by mathematically combining the standard uncertainties of the many input quantities (parameters), involved in the entire radioanalytical process. This will involve making some assumptions and normally involve using typical or worst case values for a conservative estimate of the method uncertainty. Some of these input quantities, and thus the method uncertainty, vary according to analyte level or concentration in the final measured product; others do not. In some cases, the magnitude of the method uncertainty for an analyte may increase in proportion to the magnitude (concentration/activity) of any interfering radionuclide present in the final measurement product. Therefore, it is imperative that the TEC evaluate the laboratory's submitted documentation relative to this requirement, especially the information provided on method specificity, given the historical or expected interfering nuclides and the needed decontamination factors (chemical separation factors) to render a good measurement for the analyte of interest.

In evaluating the documentation relevant to meeting the method uncertainty requirement, it is important to determine if the method validation requirements stated in the SOW have been met. The TEC should review the submitted method validation documentation and verify that the method's performance meets the requirements of Table 6.1 (Chapter 6) for the specified validation level. It is important that the laboratory submit definitive documentation of method validation compliance for the method uncertainty requirement.

The method performance documentation may include documentation or data from method validation, internal or external (organization sending QC samples) QC data, external PE program data, and results of prequalifying laboratories by sample analyses. By evaluating the actual QC and PE program performance data, it can be determined if the quoted measurement uncertainty for a reported QC sample result (calculated by the laboratory) truly reflects the method uncertainty under routine processing of samples. The required method uncertainty can be viewed as a target value for the overall average measurement uncertainty for the samples at a specified analyte concentration. It is important that the precision, as calculated from repeated measurements, is consistent with the laboratory's stated measurement uncertainty for a given sample result whose analyte concentration is near the specified concentration. If the quoted measurement uncertainty of a QC or test measurement is quoted to be ± 10 percent and QC or PE program data indicates a data set standard deviation of ± 20 percent, then the laboratory may not have identified all possible uncertainty components or may have underestimated the magnitude of a component.

Quantification Capability

A requirement for the quantification capability of a method and the required method validation criteria may be specified in a SOW. The quantification capability, expressed as the minimum quantifiable concentration (MQC), is the smallest concentration of the analyte that ensures a result whose relative standard deviation is not greater than a specified value, usually 10 percent.

The project manager or TEC should review available documentation on the method to determine if the laboratory can meet the method quantification requirement. Method validation documentation sent by the laboratory should demonstrate explicitly, or by extrapolation, that the method, using certain input quantities and their uncertainties, can meet the quantification requirement. The method validation acceptance criteria presented in Section 6.6 have been formulated to evaluate the MQC requirement at the proper analyte concentration level, i.e., action level or other specified analyte concentration.

Some projects may send performance testing material spiked at the MQC level as a more in-depth verification of the compliance with this requirement. Laboratories may also submit documentation for internal QC or external PE program results that cover the MQC value. The TEC should evaluate the reported results to determine if the MQC requirement can be met.

DETECTION CAPABILITY

A radiochemical method's detection capability for an analyte is usually expressed in terms of minimum detectable concentration (MDC) or activity (MDA). Chapter 19 provides the definition and mathematical equations for the MDC[1] and MDA. A MDC requirement for each analyte/matrix combination may be stated in a SOW. Any proposed method should document the basis and equation for calculating the MDC. The supporting documentation on the method should contain the input quantity values that may be entered into the MDC equation to calculate the detection capability under a variety of assumptions. The TEC should evaluate the assumptions and parameter values for reasonableness and practicality. This evaluation is especially important for recently validated methods that have a limited routine processing history. MARLAP recommends that the TEC perform an independent calculation of the method's MDC using laboratory-stated typical or sample-specific parameters.

When the proposed method has been validated recently or previously used on similar projects, sufficient data should exist that either are directly related to testing the method's detection capability or can be used to estimate the method's detection capability. Any data submitted that document direct testing of the method's detection capability should be reviewed for appropriateness or applicability, reasonableness, and accuracy. If method detection testing is performed, it normally will be for one analyte concentration level or value. It should not be expected that the MDC testing process included varying the magnitude of the method's many parameters over a wide range.

The reported quantitative results of the blanks can be used to estimate the MDC to within a certain degree of confidence (for most methods). At or below the MDC value, the majority of the measurement uncertainty typically is due to the Poisson counting uncertainty. For well-controlled

[1]The MDC should not be confused with the concept of the critical value (Chapter 20).

methods, the uncertainties of the other method parameters (input quantities), such as sample weight, detection efficiency, and chemical yield, may range up to 10 percent. Therefore, a simple rule of thumb to estimate the MDC for most methods involves reviewing the measurement uncertainty for the reported blank results. If the blanks were analyzed to meet the MDC requirement, then the reported MDC (based on blank and sample paired observations) for most methods should be between 3 and 4 times the measurement uncertainty of the blank when the background counts (per measurement interval) are greater than 10. It is more complicated to estimate the MDC for methods that use low background detectors (such as alpha spectrometry) having background counts less than 10 per counting interval. The TEC should evaluate the blank data to determine the reasonableness of the quoted MDC values. These rules of thumb can be applied to actual samples when the quoted analyte concentration value is less than two times its associated combined standard uncertainty value.

APPLICABLE ANALYTE CONCENTRATION RANGE

The applicable analyte concentration range can vary substantially depending on whether the project deals with process waste streams, environmental remediation or monitoring, or environmental or waste tank characterization research. The proposed method being evaluated should provide accurate results over the analyte concentration range stated in the SOW. Acceptable analytical results used in this context means consistent method uncertainty (at a given analyte concentration) and without significant bias. The range may be over several decades, from a minimum value (the MDC for some projects) to 100 times the action level or MQC.

Due to the effects of the Poisson counting uncertainty, most methods will provide more precise results at higher analyte concentration levels compared to those concentration levels near zero. At concentration levels near zero, background effects will render the results less precise. If the background (instrument or ambient levels of analyte in the matrix) is not well characterized, a bias may also exist. For projects or programs (environmental characterization research) that have no action level requirement, the lower portion of the required concentration range or the MDC requirement may be most important. For those situations, particular emphasis should be placed on evaluating method and reagent blank data (i.e., net results that take into account inherent analyte content in the reagents or tracers) to ensure that a bias does not exist. Refer to Section 7.2.2.5, “Bias Considerations,” on page 7-13 for additional guidance.

Typically, radiation detection systems are linear in signal response over a very large range of count rates. However, depending on the magnitude of the chemical or radionuclide interferences in the sample, the method may not produce linear results over the entire application range. Therefore, it is critical that when a mixture of radionuclides is present in a sample, the method must provide sufficient “analyte selectivity/isolation or impurity decontamination” to ensure valid results and “method linearity.” In some cases, such as that for pure beta-emitting analytes, the degree of needed decontamination from other interfering nuclides may be as much as six orders of magnitude.

There are several sources of information available from the laboratory that should be reviewed and possibly evaluated to ensure the method is capable of meeting this MQO. These include method validation documentation, previous projects or experience using the method, PE program results, internal and external QC sample results, and prequalifying test samples. When evaluating the data, the TEC should evaluate the method's performance as a function of analyte concentration with and without interferences. However, this evaluation would be most valid when the samples were processed to the same MQO (especially MDC or MQC), a situation that may not be realistic for different projects. If the MDC requirement results in a longer counting time from one project to another, there may be an impact on the method's uncertainty for a given analyte concentration due to difference in the Poisson counting uncertainty. Bias typically is not affected by increasing the counting time. A graphical plot of this data would be visually helpful and may be used to determine if the method uncertainty requirement would be met at the action level (extrapolation may be necessary).

METHOD SPECIFICITY

Method specificity refers to the ability of the method to measure the analyte of concern in the presence of other radionuclide or chemical interferences. The need for or degree of method specificity depends on the degree or magnitude of the interferences and their effect on the ability to measure the analyte of interest. Gross alpha, beta, and gamma-ray methods (which do not have fine resolution) are considered to be methods of low specificity and are used when individual nuclide specificity is not possible or needed. Radiochemical methods involving sample digestion, purification and decontamination steps followed by alpha spectrometry, such as for ^{239}Pu in soil, are considered methods of high specificity. However, the relative degree of specificity of these nuclide specific methods depends on the number of analyte isolation and interference decontamination steps. High-resolution gamma-ray spectrometry employing a germanium (Ge) detector is considered to have better specificity than the lower resolution sodium iodide (NaI) gamma-ray spectrometry.

The TEC should evaluate the proposed methods for adequacy to meet the specificity requirements stated in the SOW. As mentioned in Chapter 6, methods of low specificity, such as gross radiation detection methods, may be proposed if the methods meet the MQOs. For example, when a single analyte having a relatively elevated action level needs to be evaluated, such as ^{137}Cs in soil at an action level of 222 Bq/kg (6 pCi/g), then a method with less specificity (gross counting methods for gamma-ray or beta emitting nuclides) may be sufficient to meet the MQOs. For this example, a less expensive NaI gamma-ray spectrometric analysis with a lower resolution capability may be more desirable compared to a more costly high resolution germanium gamma-ray spectrometric analysis. If greater method specificity for a certain analyte/matrix combination has been required in the SOW, then a high resolution non-destructive sample analysis method (such as high resolution gamma-ray spectrometry) or a destructive sample analysis by a detailed radiochemical method would be appropriate. For proposed methods of high specificity, it is important that the TEC review and evaluate the basic purification and decontamination steps of

the method, or the resolution of the radiation detection system, for adequacy in relation to the expected mixture of analytes and interferences. For radiochemical methods, the TEC may be able to estimate the needed distribution/partition coefficients, extraction and solubility factors, etc., of the various purification steps and compare the values against the needed decontamination factors for the interfering chemical or radionuclide interferences.

The adequacy of method specificity can be evaluated by the analytical results from the analysis of site-specific PT materials during method validation and/or laboratory prequalifying tests. A further discussion on the use of these materials is presented below.

METHOD RUGGEDNESS

Method ruggedness refers to the ability of the method to produce accurate results over wide variations in sample matrix composition and chemical and radionuclide interferences, as well as when steps (such as pH adjustments) in the method are varied slightly by the analyst. For some projects, the matrix composition and level of analyte or interferences may very dramatically in a given project.

Ruggedness studies have been defined by EPA (2002). A testing protocol for method ruggedness has been outlined by the American Public Health Association (APHA). Some laboratories may have developed methods according to the APHA protocol for method ruggedness or are using methods contained in standards methods (APHA, 1998). Documentation on any internal ruggedness study may be available from the laboratory.

As mentioned in Chapter 5 and 6, the use of site-specific PT materials is a means of testing the ruggedness of a method for a defined project. If ruggedness and method specificity are concerns due to the sample matrix of a defined project, then a variety of site-specific performance testing materials should be sent to the laboratory as part of the prequalification process or as a method validation requirement. National PE programs, such as DOE's Multiple Analyte Performance Evaluation Program (MAPEP) and Quality Assessment Program (QAP), use generic PT materials and may not be applicable or representative of the matrices for a defined project. The results of the prequalifying or method validation processes using site-specific PT materials should be evaluated by the TEC to determine the adequacy of the method to meet this MQO parameter. If the sample matrix and analytes are fairly standard, then no other evaluation of the available information may be necessary.

7.2.2.5 Bias Considerations

The method proposed by the laboratory should produce analytical results that are unbiased. MARLAP considers bias to be a persistent difference of the measured result from the true value of the quantity being measured, which does not vary if the measurement is repeated. Normally, bias cannot be determined from a single result or a few results (unless the bias is large). Bias may

be expressed as the percent deviation in (or deviation from) the "known" analyte concentration. Since bias is estimated by repeated measurements, there will be an uncertainty in the calculated value. It is incumbent upon the project manager or TEC to evaluate the proposed methods for possible bias over the applicable analyte concentration range. A laboratory should eliminate all known biases before using a method. However, there may be circumstances, such as the processing of site-specific sample matrices, that may produce some inherent bias that is difficult to assess or correct in a reasonable time or economical fashion. For the methods proposed, the project manager must determine if the magnitude of the bias will significantly affect the data quality.

A bias can be positive or negative. Methods may have a bias at all analyte concentration levels due to the improper determinations of chemical yield, detector efficiency or resolution, subtraction of interferences, and improper assumptions for the analyte's half-life or an emission branching ratio. When reporting an analyte concentration based on a decay progeny analysis, improper ingrowth assumptions may lead to a bias.

MARLAP recommends that the project manager or TEC evaluate the available data provided by the laboratory or from performance evaluations for bias, based on multiple analyses covering the applicable analyte concentration range. One means of estimating a bias is through the evaluation of external PE program data.[2] For proper evaluation of the PE program sample results, it is essential that the PE program provider use sample preparation techniques that will produce performance testing (PT) samples (or a sample distribution) having insignificant "within or between" sample analyte heterogeneity and whose analyte concentrations are accurately known.

For the purpose of evaluating whether a laboratory method has an observable bias based on multiple laboratory internal QC samples (matrix or method spikes) or external PE program samples, the following equations can be used:

$$D_i = 100 * \left(\frac{X_i - Y_{i\ \text{Known}}}{Y_{i\ \text{Known}}} \right) \tag{7.1}$$

where D_i is the percent deviation, X_i is an individual analytical result and $Y_{i\ known}$ is the "known" value for the sample analyzed. The D_i should be determined for each test sample in the data set. The mean percent deviation for the method for a series of analyses in the data set can be estimated by the equation:

[2] In order to standardize against the national standard (NIST), an external performance evaluation program should be implemented by a well-qualified provider that has standardized its reference materials to NIST or is participating in a NIST traceability program

$$\bar{D} = \frac{\sum_{i=1}^{N}(D_i)}{N} \quad (7.2)$$

Refer to various references (ASTM D2777, NBS 1963, Taylor 1990) for applicable tests that may be performed to determine if there is a statistical difference at a given significance level.

There may be a negative or positive bias at low analyte concentrations due to the improper determination of the appropriate detector background or analytical blank value. For an individual blank result, the result (net activity or concentration value) would be considered to be a statistically positive value if the magnitude of its value is greater than 1.65 times the quoted measurement uncertainty. An older, much less conservative approach was to consider a reported value as a positive value when the magnitude of a result was greater than 3 times the measurement uncertainty.

Since the measurement process is statistical in nature and involves the subtraction of an appropriate background or blank which also has an uncertainty, there is a 50 percent probability (half of the results) that the analytical result for a blank sample will have a negative magnitude, e.g., -1.5 ± 2.0. For an individual blank measurement, the measurement may be considered to be problematic when the negative magnitude is greater than 2 or 3 times the measurement uncertainty.

For most radionuclides, other than those that are naturally occurring, the major source of a positive blank is from contamination, either cross-contamination from other samples or dirty glassware during sample processing or from tracer impurities. A poor estimate of the instrument background or ambient analyte levels in the matrix/reagent can lead to results being too negative in magnitude. A statistical test should be performed on a series of the data results to determine if there is a negative bias. The relative importance of the negative bias depends on the magnitude of the negative bias, magnitude of the action level and type of project.

7.3 Initial Evaluation of a Laboratory

The basic information to be considered in the initial evaluation of a laboratory has been summarized according to major categories in Figure 7.1. Not all categories will be discussed in detail as subsections. Some categories may be grouped and discussed under a single generic subsection heading. In order to allow for flexibility, no definitive guidance or detailed acceptance criteria for the parameters under discussion will be provided.

7.3.1 Review of Quality System Documents

A radiochemical laboratory providing usable analytical data should have a quality manual. A review of this document by a knowledgeable evaluator can reveal a great deal about the quality

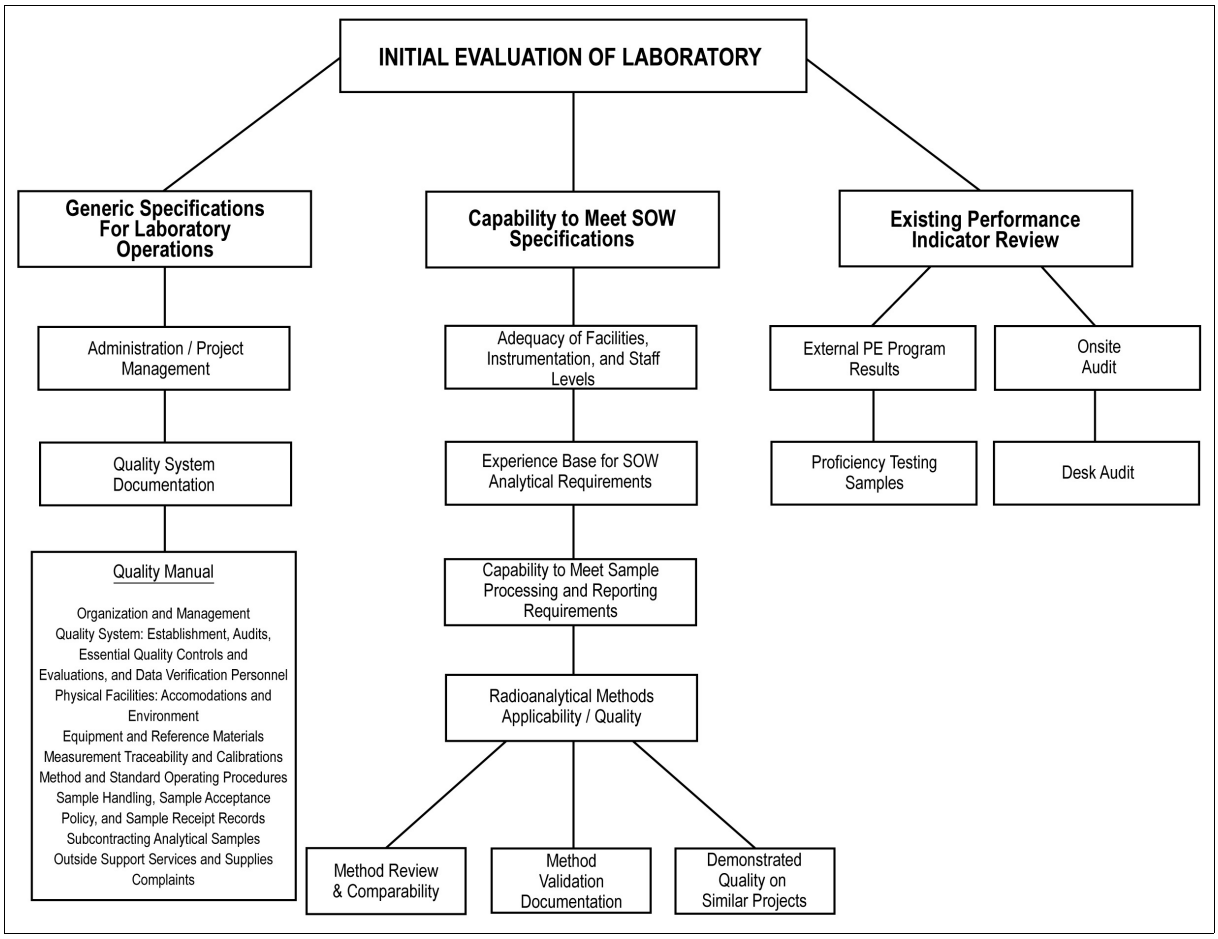

FIGURE 7.1 — Considerations for the initial evaluation of a laboratory

and acceptability of the laboratory relative to the work to be performed. A well-developed quality manual contains a description of the quality system and descriptive material covering most other aspects of a laboratory's operation. The standard operating procedures, method documentation, list of instrumentation, and personnel resumes should be reviewed. For some projects, the project manager may require the laboratory to develop a specific project quality plan, system, and manual. The following items, taken from the NELAC *Quality Systems* (NELAC 2002), should be discussed at a minimum:

- Organization and management
- Quality system establishment, audits, essential quality controls and evaluation, and data verification
- Personnel (qualifications and resumes)
- Physical facilities (accommodations and environment)
- Equipment and reference materials
- Measurement traceability and calibration
- Test methods and standard operating procedures (methods)

- Sample handling, sample acceptance policy and sample receipt
- Records
- Subcontracting analytical samples
- Outside support services and supplies
- Complaints

The laboratory evaluation should involve a review of the quality system documents for completeness, thoroughness, and clarity.

7.3.2 Adequacy of Facilities, Instrumentation, and Staff Levels

Many factors enter into a laboratory's ability to meet the analytical requirements of a SOW. The resources and facilities of a laboratory may become stretched depending on the number of clients, the analytical services needed, and the deadlines of the committed work activities. Some SOWs may request information about the current workload of the laboratory and available facilities, staff and nuclear instrumentation for the specified work scope. The resources needed will vary considerably depending on the analysis and number of samples: from minimal bench space, hoods, and nuclear instrumentation for fairly simple gross analyses to maximum bench space, hoods, staff, and nuclear instrumentation for low-level analyses of soil. In addition, the laboratory capacity also depends on the number of samples that are routinely processed in a batch. Various factors may control the batch size, including the hood processing area, bench space, and equipment setup, available number of radiation detectors, counting time, and half-life of radionuclide, among others.

The adequacy of the facilities, instrumentation, and staff levels can be estimated by two general mechanisms: detailed supporting information provided by the laboratory in response to the SOW and an initial onsite audit. Information received from the prospective laboratory may provide an estimate of the laboratory's resources, but an initial onsite audit verifies the actual existence and maintenance of the resources.

7.3.3 Review of Applicable Prior Work

If required in a SOW, a laboratory will provide a list of clients for whom radioanalytical services had been performed that are considered comparable in terms of work scope, DQOs, MQOs, APSs, and project type. A written or oral verification of the client list should be performed. As part of the verification process, the following items related to adherence to contract or project requirements should be discussed and documented:

- Radionuclides analyzed;
- Sample matrices types;
- Laboratory capacity (number of samples per week or another time period);
- MQO for method uncertainty, detection and quantification capability;

- Radiological holding times;
- Sample turnaround times;
- Corrective actions; and
- Communications related to schedule, capacity, or quality issues.

It should be noted that under performance-based contracting, a laboratory's prior work for an agency should be considered, either as a positive or negative performance weighting factor, when scoring a laboratory's performance during the technical evaluation process.

7.3.4 Review of General Laboratory Performance

Some laboratories compile a semiannual or annual QA report summarizing the internal QC sample results for the methods used during a given time period, as well as an internal quality assessment report summarizing the internal and external audit findings and corrective actions taken. Although the laboratory's internal quality criteria for a given radionuclide/matrix may be different from the project MQOs, the internal QC sample results can be used to gauge the laboratory's performance capabilities. If these documents are available, they should be reviewed for documentation of process control and pertinent quality parameters such as bias, precision, unusually high number of positive blank detection, chemical recoveries, turnaround times, number of recurring deficiencies or findings, and corrective action effectiveness.

7.3.4.1 Review of Internal QC Results

A quality assessment report may contain a summary of various QA-related activities, including internal audits and surveillance, report of conditions adverse to quality, investigation requests, corrective actions, and the results of external PE programs and internal QC samples. The content and frequency of the reports normally are outlined in the laboratory's quality manual. Frequently, this type of quality assessment report may be submitted with the laboratory's response to the RFP without request. The TEC may want to specifically request such a report when available.

When the laboratory's quality system is effectively implemented, the information contained in these QA reports can be used not only to gauge the quality of the analyses but also the effectiveness and timeliness of such quality system activities as identifying conditions adverse to quality, controlling and monitoring the radioanalytical quality using internal QC samples, and corrective actions. The internal QC sample results can be used to gauge the laboratory's performance capability. Results of the QC samples for a radionuclide and sample matrix should be reviewed for both the batch QC samples and single- or double-blind samples submitted by the QA officer. Batch QC samples typically include laboratory control samples, method blanks, matrix spikes, splits, and duplicates. Such parameters as acceptable percent deviation for spiked samples, acceptable precision as measured by duplicate sample analyses, false nuclide detection, positive blanks, and compliance to internal quality requirements should be reviewed, depending on the

type of QC sample. The single- and double-blind samples submitted independently by the QA officer are considered more operationally independent than the batch QC samples.

When quality problems are observed by the reviewer, it is important to check if the laboratory's quality system also has found and reported the same problem and whether an investigation or corrective action has been undertaken.

Additional specific guidance is provided in Chapter 18 (*Laboratory Quality Control*) on evaluating internal QC samples to meet internal laboratory QC performance criteria. It is recommended that the project managers review this chapter to gain a perspective on how to use reported internal QC results to gauge a laboratory's potential to meet project MQOs.

7.3.4.2 External PE Program Results

Typically, a laboratory's performance or capability to perform high quality radiochemical analyses can be evaluated through two external PE program mechanisms. The first mechanism, which may not be available for all projects, is the submittal, as an initial laboratory evaluation process, of project-specific PT samples prepared by the organization or a contracted source manufacturer. When previous knowledge or experience exists, well-characterized site-specific matrix samples containing the nuclides of interest can be used. This approach can use site-specific matrix materials for background samples or for samples spiked with target analytes. For this evaluation mechanism, and depending on the number and type of samples, the laboratory's capability to meet all proposed project MQOs and quality performance specifications may be evaluated.

The second mechanism, available to most projects, is the laboratory's participation in government or commercial PE programs for radiochemical analyses. Each PE program has its own acceptable performance criteria related to a laboratory's bias with respect to the PE program's "known" analyte concentration value. Acceptable performance criteria are established for each nuclide/matrix combination. A PE program may also evaluate a laboratory based on a false positive analyte detection criterion. Typically, the laboratory's performance data in government PE programs are provided in reports available to the public.

The project manager should be aware that the acceptable performance criteria used by the PE programs may be inconsistent with or more lenient than the MQOs of the project. The laboratory's performance should be evaluated in terms of the established MQOs of the project rather than a PE program's acceptable performance criteria. In some cases, the laboratories could be ranked as to their level of performance in these programs.

7.3.4.3 Internal and External Quality Assessment Reports

Most laboratories undergo several external and internal QA audits per year, with resultant audit reports. Typically, a summary of the findings and commitments of internal and external quality audits or assessments are tracked on some type of QA database as part of the laboratory's corrective action process. Access to the audit reports or database information may be limited. This information is not normally requested as part of the RFP process, nor do most laboratories submit such information with their response to an RFP. Therefore, obtaining previous QA audit information from a laboratory outside a formal, external, onsite audit process may be limited.

7.3.5 Initial Audit

An initial assessment or audit may be performed to provide assurance that a potentially selected laboratory is capable of fulfilling the project requirements in accordance with the SOW. Essentially, the objectives of an initial audit are twofold. The first objective is to verify that what the laboratory claims in response to the SOW or RFP, such as the various quality and safety programs, are being correctly and fully implemented, and when used during the project period, will ensure that stipulated requirements will be met. The second objective is to determine if the laboratory has the instruments, facilities, staffing levels and other operational requirements available to handle the anticipated volume of work. In other words, is the laboratory's proposal realistic when compared to the actual facilities? To answer this question, auditors will be looking to see whether a candidate laboratory has all the required elements to meet the project needs.

Detailed guidance and information on what should be evaluated in an initial audit has been provided in Appendix E, Section E5.5 and Table E7. This section also contains recommendations on the key items or parameters that should be reviewed during the initial audit. Depending on the project, other quality or operational parameters/requirements (such as requirements related to chemical speciation or subsampling at the laboratory) not covered in Appendix E should be included in the initial audit plan.

7.4 Ongoing Evaluation of the Laboratory's Performance

The evaluation framework presented here is intended to be sufficiently generic to cover the operations of a laboratory performing work according to a SOW as recommended in Chapter 5. As described in MARLAP, MQOs are a key component of the SOW. Therefore, the sample schedule, analyses to be performed, MQOs, and other analytical requirements have been defined. The methods selected by the laboratory have been demonstrated to meet the MQOs and have been approved by the project manager. In addition, the laboratory and its programs should have undergone an initial audit to ensure that the laboratory has met or is capable of meeting project requirements, including sample processing capacity, sample TATs, deliverables for analytical reports, etc. This would include maintaining a satisfactory quality system that includes

monitoring and controlling the radioanalytical processes through an instrument and internal sample QC program and the acceptable performance in an external PE program.

The ongoing evaluation of a laboratory's performance includes the evaluation of the method applicability or the quality of the data produced, and assessing the laboratory's quality system and operations through onsite or desk audits or assessments. The continued method performance can be evaluated through the laboratory's internal sample QC program, a possible external QC program maintained by the project manager, or an external PE program. It should be noted that samples used to control and monitor the quality of laboratory analyses have been defined according to their use. For example, batch or external QC samples are used to control as well as monitor the quality of the analytical process (the process can be stopped immediately if the QC sample results indicate that the process is outside appropriate SOW specifications or laboratory control limits). As defined previously, PT samples are used to compare the performance of the radioanalytical processing to some acceptance criteria but are not used to control the process.

The ongoing evaluation of the laboratory quality system and operations is accomplished through a visit to the laboratory or by a desk audit (the review of records and data from the laboratory). These audits or assessments are more focused on whether the laboratory is meeting project specifications rather than whether the laboratory has the capability to meet project or SOW requirements.

Once a laboratory has initiated work on a project, the laboratory's performance should be evaluated for the duration of the project. The quality of the radioanalytical measurements, as well as the pertinent key operational aspects of the laboratory, should be evaluated against the requirements of the MQOs and SOW. Both the quantitative and qualitative measures of laboratory performance should be evaluated on a continual basis. In addition, the operational aspects of the laboratory germane to the effective implementation of the project requirements should be evaluated/monitored on a continual basis.

7.4.1 Quantitative Measures of Quality

The laboratory's ongoing demonstrated ability to meet the MQOs and other APS requirements can be evaluated through various quantitative measures using internal QC data and external PE program QC data. From these data, quantitative tests, as outlined in Appendix C can be used to measure and monitor the MQO parameters on a short-term basis. Also, the QC and PE program data can be used to evaluate the laboratory's performance, on a long-term trending basis, in meeting other quality related parameters such as bias and precision, unusually high number of positive blank detection, false nuclide detection, MDC or MQC adherence, radiological holding times, etc. The following subsections will discuss the use of data from these samples to evaluate the laboratory's radioanalytical quality with respect to the requirements.

7.4.1.1 MQO Compliance

MARLAP recommends that project-specific MQOs be established and incorporated into the SOW for laboratory radioanalytical services. Appendix C provides guidance on developing the MQOs for method uncertainty, detection capability, and quantification capability. Establishing a gray region and action level are important to the development of the MQOs. For certain research programs and characterization studies, the concept of an action level may not be applicable. For these studies or programs, the MDC requirement and restrictions on the frequency of false positive detections may be more important. As such, the project planning team for these programs should establish the basis for their own MQOs and develop tests to evaluate a laboratory's performance to meet the requirements. These tests may be different from those presented below.

MARLAP recommends that a MQO for method uncertainty be established for each analyte/matrix combination. The method uncertainty is affected by laboratory sample preparation, subsampling, and the analytical method. In the absence of other information, the required method uncertainty (u_{MR}) at the upper bound of the gray region (UBGR) may be defined as:

$$u_{MR} = \frac{\Delta}{10} \tag{7.3}$$

where u_{MR} is the method uncertainty and Δ is the width of the gray region (difference between the upper and lower bounds of the gray region) as defined in Appendix C. In terms of the relative fraction of the upper bound of the gray region (action level), φ_{MR}, is defined:

$$\varphi_{MR} = \frac{u_{MR}}{\text{UBGR}} \tag{7.4}$$

The following subsections describe methods to quantitatively monitor a laboratory's performance relative to meeting this principal MQO through the use of internal or external batch QC samples. In some cases, the laboratory's internal quality program may have more restrictive quality control limitations for method performance compared to the proposed control limits used by the project manager to monitor adherence to the MQO for method uncertainty. Evaluation of the laboratory's performance in NIST-traceable external PE programs will determine the degree of bias of the laboratory's method with respect to the national standard, as opposed to the determination of the laboratory's internal bias through the use of internal QC samples. The tests presented assume that all known internal (related to QC values and calibrations) and external (calibration differences with respect to the national standard) biases have been defined and eliminated and, as such, the difference between the measured result and the "expected known" value is a result of the method uncertainty only.

USE OF INTERNAL QC SAMPLE RESULTS

For most projects, the SOW will specify that the laboratory incorporate internal QC samples within a defined batch of samples. The QC samples may include a laboratory control sample, sample duplicates, a matrix spike sample and a method or reagent blank, or both. Appendix C provides examples on the use of the following quantitative tests to measure a laboratory's performance in meeting the MQO for method uncertainty.

Quality Performance Tests and Acceptance Criteria for Quality Control Samples

Laboratory Control Sample (LCS). The analyte concentration of an LCS should be high enough so that the resulting Poisson counting uncertainty is small and the relative uncertainty limit φ_{MR} is appropriate with respect to the action level and the spike concentration chosen. The percent deviation (%D) for the LCS analysis is defined as

$$\%D = \frac{\text{SSR} - \text{SA}}{\text{SA}} \times 100\% \tag{7.5}$$

where

SSR is the measured result (spiked sample result) and
SA is the spike activity (or concentration) added.

It is assumed that the uncertainty of SA is negligible with respect to the uncertainty of SSR. Refer to Appendix C for the basic assumption and limitation of this test. For long-term trending, the %D results should be plotted graphically in terms of a quality control chart as described in Chapter 18. The warning and control limits on %D are summarized below:

Laboratory Control Samples

Statistic:	%D
Warning limits:	$(\pm 2\varphi_{MR}) \times 100\%$
Control limits:	$(\pm 3\varphi_{MR}) \times 100\%$

Duplicate Analyses. The acceptance criteria for duplicate analysis results depend on the analyte concentration of the sample, which is estimated by the average $\bar{x}$ of the two measured results x_1 and x_2.

$$\bar{x} = \frac{x_1 + x_2}{2} \tag{7.6}$$

When $\bar{x} < UBGR$, the absolute difference $|x_1 - x_2|$ of the two measurements is used in the testing protocol. For these tests, only upper warning and control limits are used, because the absolute value $|x_1 - x_2|$ is being tested.

When $\bar{x} \geq UBGR$, the acceptance criteria may be expressed in terms of the *relative percent difference* (RPD) defined as

$$\text{RPD} = \frac{|x_1 - x_2|}{\bar{x}} \times 100\% \qquad (7.7)$$

The requirements for duplicate analyses are summarized below.

Duplicate Analyses

If $\bar{x} <$ UBGR:

Statistic: $|x_1 - x_2|$
Warning limit: $2.83\ \boldsymbol{u}_{MR}$
Control limit: $4.24\ \boldsymbol{u}_{MR}$

If $\bar{x} \geq$ UBGR:

Statistic: $\text{RPD} = \frac{|x_1 - x_2|}{\bar{x}} \times 100\%$
Warning limit: $2.83\ \varphi_{MR} \times 100\%$
Control limit: $4.24\ \varphi_{MR} \times 100\%$

<u>*Method Blanks*</u>. When an aliquant of a blank material is analyzed, the target value is zero. However, the measured value may be either positive or negative. The applicable warning and control uncertainty limits for blank samples are defined as:

Method Blanks

Statistic: Measured Concentration Value
Warning limits: $\pm\ 2u_{MR}$
Control limits: $\pm\ 3u_{MR}$

<u>*Matrix Spikes*</u>. The acceptance criteria for matrix spikes are more complicated than those described above for the other laboratory QC samples because of the pre-existing activity that is inherent to the unspiked sample. The pre-existing activity (or concentration) must be measured and subtracted from the activity measured after spiking.

MARLAP recommends the "*Z* score," defined below, as the test for matrix spikes.

$$Z = \frac{SSR - SR - SA}{\varphi_{MR}\sqrt{SSR^2 + \max(SR, UBGR)^2}} \quad (7.8)$$

where:

SSR is the spiked sample result,
SR is the unspiked sample result,
SA is the spike concentration added (total activity divided by aliquant mass), and
max(SR,UBGR) denotes the maximum of SR and UBGR.

The warning and control limits for Z are set at ± 2 and ± 3, respectively. It is assumed that the uncertainty of SA is negligible with respect to the uncertainty of SSR. For long-term trending, the Z results should be plotted graphically in terms of a quality control chart, as described in Chapter 18.

The requirements for matrix spikes are summarized below.

Matrix Spikes

Statistic: $Z = \frac{SSR - SR - SA}{\varphi_{MR}\sqrt{SSR^2 + \max(SR, UBGR)^2}}$
Warning limits: ± 2
Control limits: ± 3

USE OF EXTERNAL PE PROGRAM AND QC SAMPLE RESULTS

Information on a laboratory's performance in an external PE program or from double-blind QC samples is very useful in monitoring a laboratory's ability to meet MQOs. A PE program will provide a snapshot in time whereas external QC samples included with samples submitted to the laboratory permit a continuous evaluation of the method's performance. When traceable to NIST, the PE program will elucidate any measurement or instrument calibration biases as related to the national standard. An external QC program may not have NIST traceability, and thus calibration biases to the national standard would not be determined.

For monitoring the performance of a laboratory using external PE program and QC sample results, the tests provided in the previous subsection ("Use of Internal QC Sample Results," page 7-25) may be used when there are sufficient data. The test equations assume that the project has an MQO for method uncertainty at a specific concentration. In addition, it is assumed that the Poisson counting uncertainty for the radioanalysis of these samples is minimal.

Results from PE Programs

In many SOWs, the laboratory is required to participate in a recognized PE program for the nuclides and media of interest. In some cases, a certificate of participation may be needed as part of response to the RFP. However, it also should be noted that although a laboratory may meet performance acceptance criteria for an external PE program, this fact may have no bearing on whether the method will meet the MQOs of the SOW.

Monitoring ongoing laboratory performance is limited due to the minimum frequency of testing of the PE program, i.e., usually quarterly or semiannually. Some PE programs require multiple measurements to estimate precision but most only request a single result be reported. In addition, the concentration of the analyte typically never approaches an action level value and the media used are not site specific. For PE program samples, when possible, the laboratory should analyze a sample to reach a 1σ Poisson counting uncertainty that is less than five percent.

Multiple Analyses and Results

When a PE program requires the analysis of multiple samples, the laboratory's measurement precision and bias (to a "known value") at the analyte concentration may be estimated and reported by the PE program provider. When only duplicates sample results are reported, then the tests for laboratory control samples and duplicate analyses given in the previous section should be used. The duplicate analysis test can be used as is, but the laboratory control sample test should be evaluated based on the mean of the duplicate results. By using the mean of the two results, the LCS test provides a better estimate of any laboratory measurement bias with respect to the PE program provider. As discussed in Appendix C, the measurement (combined standard) uncertainty of each measured result value should be smaller than the required u_{MR} or φ_{MR}.

Results from External QC Samples

The project manager may elect to establish an external QC program wherein QC samples are submitted to the laboratory with each batch of routine samples for the purpose of "controlling," rather than monitoring, the quality of the analytical processes. The types of QC samples may include matrix spikes, blanks, and possibly duplicates if prepared under controlled and exacting protocols. An agency may use a qualified reference or monitoring laboratory (ANSI N42.23) to prepare the performance testing materials. When available, these QC samples may be prepared from site-specific materials.

When acceptance criteria are not met, the organization may issue a stop-work order and request corrective actions and reanalysis before routine processing can resume. In order to do this, the SOW must define the performance acceptance criteria and stipulate that the agency or organization has the right to stop laboratory processing when the performance requirements are not met. This application is not widespread but may have merit for certain project types. For

example, research or national monitoring programs may monitor groundwater for specific naturally occurring radionuclides at state-of-art detection levels. For these programs, frequent false positive results, due to the application of incorrect instrument background or an analytical blank to the analytical result, would be unacceptable. Rather than permit a high rate of false positive results to continue, the agency can use the external batch QC samples to detect problems early and have the laboratory discontinue sample processing until a root cause is discovered and a corrective action undertaken. Non-conformance of a single analysis to performance criteria would not warrant the issuance of a stop work order unless a severe blunder has occurred. Typically, a certain amount of statistical trending of the data is in order to truly elucidate deficiencies.

Since the number of QC samples is similar to the recommendations for the laboratory's internal batch QC samples, there should be sufficient data for trending. The statistical tests provided in the section on "Use of Internal QC Sample Results," beginning on page 7-25, may be applied to these QC samples.

7.4.1.2 Other Parameters

The laboratory's performance in meeting the requirements for the other APSs that are listed in the SOW should be evaluated quantitatively when possible. In some cases, the information needed to perform the evaluations may be found in the final analytical results data package. For certain types of evaluations, a follow-up onsite or desk audit may be needed to complete the evaluation, e.g., a review of logbooks on unique processes or software algorithms and the analytical data base for proper spectral resolution.

RADIOLOGICAL HOLDING AND TURNAROUND TIMES

The data packages or analytical results report should contain the sample collection (reference), sample analysis, and reporting dates. From this information, the radiological holding and sample processing TATs can be calculated and compared against requirements. When a method uses a decay progeny to measure the analyte of interest (^{222}Rn to measure ^{226}Ra), the decay of the parent nuclide and ingrowth of the decay progeny are important parameters for evaluation. Unless requested in the SOW, most laboratories do not report the ingrowth factor as a standard output. Therefore, the information on the sample-specific ingrowth factor may not be readily available and reported only on the data sheets or during audits. When required, these time related requirements will be evaluated for compliance during data verification and validation.

CHEMICAL YIELD

When appropriate, the SOW may specify limits on the chemical yield for each analyte. For radionuclides, this requirement typically is related to the provision of robust or rugged methods so that extreme yields become flags indicating potential problems. Wide swings in the chemical

yield may be indicative of method's difficulty handling matrix or radionuclide interferences. The data packages or analytical results report should contain the chemical yield for each analyte listed. This reported value can be compared to the SOW yield limit. When required, these requirements will be evaluated for compliance during data verification and validation.

SPECTRAL RESOLUTION

Problems with spectral resolution of gamma-ray and alpha spectra cannot be evaluated through a review of the analytical results report. If spectral resolution limits have been stated in the SOW, the evaluator should review and evaluate each sample spectrum against the SOW limit. Spectral information may be available in data packages when required or may be obtained during audits.

During an initial audit, a preliminary evaluation of the method's SOP and review of past performance data for spectral resolution should be undertaken. The TEC may want to determine the baseline or typical spectral resolution for the radiation detection systems that will be used in the analysis of project samples. Trends of the spectral resolution of each detection system during the conduct of the project may be used to determine compliance with a spectral resolution specification.

7.4.2 Operational Aspects

Once a laboratory begins providing radioanalytical services, certain operational aspects need to be reviewed and evaluated periodically to determine if the laboratory is maintaining project requirements or if new problems have occurred. It is also important to ensure that the laboratory has been properly maintained and is operated and managed in a manner that will not create a liability to any client. Many of the operational areas that were discussed in Sections 7.3.1 and 7.3.2 for the initial evaluation of a laboratory also should be evaluated periodically to ensure commitments are being met. The audit frequency varies according to the organization and the extent of the project or contract. Desk audits can be conducted more frequently than onsite audits because they require fewer resources. However, not all operational aspects may be reviewed during desk audits. The operational aspects that may be considered during desk and onsite audits are presented below.

7.4.2.1 Desk Audits

A desk audit is conducted as an off-site activity, usually by a technical representative of the project manager. A radioanalytical specialist should review all technical aspects of the desk audit, including method and calculation (data reduction) changes, method performance, instrument recalibrations, corrective actions, and case narratives. The desk audit is most useful when performed periodically to monitor certain activities or programs following an extensive onsite laboratory audit. However, for some smaller projects, the desk audit may be the only

assessment mechanism used to monitor the laboratory's operations. The desk audit may be used to review or monitor the following operational aspects or items:

- Organization and Management
  - Changes in key personnel
  - Reassignments

- Quality System
  - Internal and external audits conducted, including laboratory certification audits
  - Corrective action implementations
  - Quality control and performance evaluations
    - Instrument and batch sample QC results
    - External PE program results
  - Laboratory data verification (narrative status reports)
  - Additional method validation studies

- Certificates, licenses, equipment, and reference materials
  - Standard and tracer certificates
  - New and updates to instrument calibrations
  - Instrument repairs and new instruments put into service
  - NRC/State radioactive materials licence updates
  - State or EPA drinking water certification status changes

- Personnel
  - Updates to staff qualification/proficiency for methods
  - Updates to staff training files
    - Radiation and chemical safety
    - Quality assurance
    - Technical principles
    - Hands-on training records

- Radioanalytical Methods and Standard Operating Procedures
  - Updates to methods and SOPs
  - Technical basis for updates
  - Detection limits or method uncertainty studies

- Sample Receipt, Handling and Disposal
  - Sample receipt acknowledgment
  - Chain-of-custody
  - Sample- and waste-disposal tracking logs and manifests

Desk audits may also be used to review the data packages provided by the laboratory and, periodically, to verify certain method results by hand calculations. In addition, verification of compliance to radiological holding and turnaround times may be performed during the desk audit. In the absence of a full data verification and validation program (Chapter 8), the desk audit may be used to periodically evaluate the detailed instrument and data reduction reports of the data packages for method adherence, technical correctness and valid application.

7.4.2.2 Onsite Audits

The onsite laboratory audit is more comprehensive and resource intensive than a desk audit. An onsite audit typically is conducted to assess, periodically and in depth, a laboratory's capability to meet project requirements. Section E.5.5 of Appendix E provides guidance on the conduct of an initial onsite audit during a contract award process. EPA (1997) provides limited guidance on the conduct of an audit for a radiological laboratory. NELAC (2002) provides some generic guidance on laboratory assessments, although not specifically for a radiological laboratory.

Onsite audits usually cover the operational aspects delineated in Section 7.4.2.1 and also provide an opportunity to evaluate the physical conditions at the laboratory, in terms of adequacy and upkeep of the facilities, and the full application or conduct of programs and resources. Information sent in data packages or submitted for desk audits can be confirmed or verified during an onsite audit. Furthermore, an onsite audit permits the tracking of a sample from receipt through processing to sample storage and disposition and can verify the related instrument and batch QC samples specific to the sample being tracked. During an onsite audit, the auditors may have interviews with the staff to gauge their technical proficiency and familiarity with methods.

For large projects, onsite audits may be formal in nature and have a predefined audit plan, which has been developed by a designated audit team, for a specific project or program. The audit team typically is comprised of qualified QA representatives and technical experts. MARLAP recommends that the audit team include a radioanalytical specialist familiar with the project's or program's technical aspects and requirements.

In addition to the items in Section 7.4.2.1 ("Desk Audits"), the following items and programs should be assessed during an onsite laboratory audit:

- Organization and Management
  - Qualifications of assigned laboratory project manager
  - Implementation of management's policy on quality
  - Timeliness of addressing client complaints
  - Timeliness of implementing corrective actions

- Physical Facilities

  - Adequacy of facilities (sample receipt, processing, instrumentation and storage areas, waste processing and storage, offices, etc.)
  - Physical conditions of facilities including laboratories, hoods, bench tops, floors, offices, etc.
  - Environmental controls, such as climate control (heating, ventilation, air conditioning) and electrical power regulation
  - Sample processing capacity
  - Sample storage conditions including chain-of-custody lockup areas and cross contamination control (separation of samples by project and from radioactive sources or wastes)

- Instrumentation and Equipment
  - Age of nuclear instrumentation and equipment
  - Functionality of nuclear instrumentation and equipment
  - Calibrations and QC logs
  - Maintenance and repair logs
  - Sample throughput capacity
  - Contamination control for radiation detectors
  - Background spectra of radiation detectors

- Methods and Standard Operating Procedures
  - Use of latest revisions of methods and SOPs (spot check method manuals used by technical staff)
  - Conformance to method application (surveillance of method implementation)
  - Effectiveness of administering the controlled method manual

- Certifications, Licenses and Certificates of Traceability
  - Ensure existence and applicability of, and conformance to, certifications and licenses
  - Noted citations during audits related to certifications and licenses
  - Ensure use of NIST-traceable materials (calibration standards)/review of vendors' report of NIST traceability

- Waste Management Practices
  - Adherence to waste management SOPs
  - Proper packaging, labeling, manifests, etc.
  - Sample storage and records
  - Training and qualification records

- Radiological Controls
  - Adherence to radiological safety SOPs
  - Contamination control effectiveness (spill control, survey requirements and adherence, posted or restricted areas, proper ventilation, cleaning policies, etc.)

- Badging and survey adherence

- Personnel
  - Number and technical depth of processing staff
  - Training files
  - Testing/qualifications
  - Personal interviews to determine familiarity of methods and safety SOPs

- Quality Systems
  - Performance indicator program (feedback from program)Quality assurance reports (QC and audits) for all laboratory processing
  - Ongoing method evaluations and validations
  - Corrective action program (effectiveness and outstanding issues for all processing; spot check for implementation of corrective actions)
  - Records/reports related to audits of vendors used by laboratory
  - Reagent control program (spot check conformance for effectiveness)
  - Audits of laboratories that are subcontracted
  - Laboratory's data verification and validation processes

- Software Verification and Validation
  - Spot review of key method calculation and data reduction programs that include MDC, MQC, and measurement uncertainty; spectral unfolding routines or crosstalk factors; application of instrument background and analytical blanks; etc.
  - Spot verification of consistency between electronic data deliverable and data packages

- Radiological Holding and Sample Turnaround Times
  - Verification of compliance to radiological holding and sample TAT specifications (spot check samples and confirm paperwork)

7.5 Summary of Recommendations

- MARLAP recommends that a radioanalytical specialist review the methods for technical adequacy.

- MARLAP recommends that the TEC perform an independent calculation of the method's MDC using laboratory-stated typical or sample-specific parameters.

- MARLAP recommends that the project manager or TEC evaluate the available data provided by the laboratory or from performance evaluations for bias, based on multiple analyses covering the applicable analyte concentration range.

- MARLAP recommends that project-specific MQOs be established and incorporated into the SOW for laboratory radioanalytical services.

- MARLAP recommends that a MQO for method uncertainty be established for each analyte/ matrix combination.

- MARLAP recommends the "*Z* score" as the test for matrix spikes.

- MARLAP recommends that an audit team include a radioanalytical specialist familiar with the project's or program's technical aspects and requirements.

7.6 References

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