3 KEY ANALYTICAL PLANNING ISSUES AND DEVELOPING ANALYTICAL PROTOCOL SPECIFICATIONS

3.1 Introduction

This chapter provides an overview of key analytical planning issues that should be addressed and resolved during a directed planning process (see Chapter 2). *A key analytical planning issue is one that has a significant effect on the selection and development of analytical protocols, or one that has the potential to be a significant contributor of uncertainty to the analytical process and, ultimately, the resulting data*. It should be noted that a key analytical planning issue for one project may not be a key issue for another project. One of the most important functions of a directed planning process is the identification and resolution of these key issues for a project. The resolution of these issues results in the development of analytical protocol specifications (APSs).

In accordance with a performance-based approach, APSs should contain only the minimum level of specificity required to meet the project or program data requirements and resolve the key analytical planning issues. While Chapter 2 provides an oversight of the project planning process, this chapter provides a focused examination of analytical planning issues and the development of APSs.

In order to assist the project planning team in identifying issues, this chapter provides a list of potential key analytical planning issues. Neither the list nor discussion of these potential issues is an exhaustive examination of all possible issues for a project. However, this chapter does provide a framework and a broad base of information that can assist in the identification of key analytical planning issues for a particular project during a directed planning process.

Analytical planning issues can be divided into two broad categories—those that tend to be matrix-specific and those that are more general in nature. While there is certainly some overlap between these two broad categories, MARLAP divides analytical planning issues along these lines because of the structure and logic it provides in developing APSs. This approach involves identifying key analytical planning issues from the general (non-matrix-specific) issues first and then proceeding on to the matrix-specific issues. Examples of non-matrix-specific analytical planning issues include sample tracking and

Contents

custody issues. These general issues are discussed in detail in Section 3.3. Examples of matrix-specific issues include filtration and preservation of water samples. Matrix-specific analytical planning issues are discussed in detail in Section 3.4. Section 3.5 provides guidance on assembling the APSs from the resolution of these issues. Section 3.6 discusses defining the level of protocol performance that must be demonstrated for a particular project, and Section 3.7 discusses incorporating the APSs into the project plan documents.

3.2 Overview of the Analytical Process

Identifying key analytical issues for a particular project requires a clear understanding of the analytical process. The analytical process (see Section 1.4.4 and Figure 3.1) starts with field-sample preparation and preservation and continues with sample receipt and inspection, laboratory sample preparation, sample dissolution, chemical separations, instrument measurements, data reduction and reporting, and sample tracking and quality control. It should be noted that a particular project's analytical process may not include all of the activities mentioned. For example, if the project's analytical process involves performing gamma spectrometry on soil samples, sample dissolution and chemical separation activities normally are not required. Each step of a particular analytical process contains potential planning issues that may be key analytical planning issues, depending on the nature and data requirements of the project. Therefore, it is important to identify the relevant activities of the analytical process for a particular project early in the directed planning process. Once the analytical process for a particular project has been established, key analytical planning issues, including both general and matrix-specific ones, can be identified.

FIGURE 3.1 — Typical components of an analytical process

3.3 General Analytical Planning Issues

There are a number of general analytical planning issues that are common to many types of projects. They may often become key planning issues, depending on the

nature and data requirements of the project, and the resolution of some of these planning issues may affect the selection of methods (see Section 6.5, "Project-Specific Considerations for Method Selection"). This section presents each planning issue as an activity to be accomplished during a directed planning process and also identifies the expected outcome of the activity in general terms. The resolution of these general analytical planning issues, particularly those that are key planning issues for a project, provides the basic framework of the APSs and, therefore, should be identified and resolved before proceeding to matrix-specific planning issues. The resolution of these issues normally results (at a minimum) in an analyte list, identified matrices of concern, measurement quality objectives (MQOs), and established frequencies and acceptance criteria for quality control (QC) samples. The resolution of matrix-specific issues, particularly those that are key issues for a project, normally provides the necessary additions and modifications to the basic framework of the APSs needed to complete and finalize the specifications. MARLAP recommends that any assumptions made during the resolution of key analytical planning issues are documented, and that these assumptions are incorporated into the appropriate narrative sections of project plan documents. Documenting these assumptions may help answer questions or help make decisions during the implementation and assessment phases of the project.

3.3.1 Develop Analyte List

From an analytical perspective, one of the most important planning issues is the target analyte list—the radionuclides of concern for the project. Note that the target analyte list may also include nonradioactive hazardous constituents, which could influence the analytical protocols, including sample collection and waste disposal issues. Although this issue probably would be dealt with by the same planning team, its discussion is outside the scope of MARLAP. For many projects, data are available from previous activities for this purpose. Four possible sources of information are (1) historical data, (2) process knowledge, (3) previous studies, and (4) information obtained from conducting a preliminary survey or characterization study. Although discussed separately in Section 3.3.3, the identification and characterization of matrices of concern often is done concurrently with the development of an analyte list.

Historical data are one source of existing information. Many activities associated with radioactive materials have been well documented. For example, activities licensed by the Nuclear Regulatory Commission (NRC) or NRC Agreement States normally generate much documentation. Chapter 3 of MARSSIM (2000) provides guidance on obtaining and evaluating historical site data.

Another source of existing information is process knowledge. Some sites are associated with a specific activity or process that involved radioactive material, where the process was well defined and the fate of the radioactive material in the process was known or controlled. Examples include uranium and rare earth ore processing, operations at Department of Energy (DOE) weapons facil-

ities, and operations at commercial nuclear power plants (see Section 6.5.2 for additional discussion on process knowledge).

A third source of existing information is previous studies. Similar projects or studies of related topics can provide valuable information during a directed planning process. Previous studies may provide useful information on background radiation. Many radionuclides are present in measurable quantities in the environment. Natural background radiation is due both to primordial and cosmogenic radionuclides. Anthropogenic background includes radionuclides that are ubiquitous in the environment as a result of such human activities as the atmospheric testing of nuclear weapons. Natural and anthropogenic backgrounds can be highly variable even within a given site. It may be important to consider the background and its variability when choosing an action level and when establishing the MQOs. Every effort should be made to obtain as much existing information as possible prior to initiating a directed planning process.

A fourth source of information is generated by conducting a preliminary survey or characterization study. This preliminary analysis may be necessary if there are little or no historical data that can help identify concentrations of radionuclides of potential concern, or if the existing data are of inadequate quality. The design of preliminary surveys or characterization studies should be part of the project planning process. The need for fast turnaround and lower costs at this stage of the project may lead to different data quality objectives (DQOs) and MQOs that are less restrictive than those used for the primary phase of the project. However, it is important that analytical requirements for the survey or study be established during the project planning process. Gross alpha, gross beta, and gamma spectrometry analyses often are used for preliminary survey or characterization studies. The benefits of performing these types of measurements include:

- Rapid analysis and short turnaround time;
- Relatively low analytical costs; and
- Ability to detect the presence of a wide range of radionuclides in a variety of matrices.

There are also limitations on the use of these analyses. These limitations include:

- No specific identification for pure alpha- or pure beta-emitting radionuclides;
- Low-energy gamma- and beta-emitting radionuclides are generally not detected; and
- Failing to detect the presence of several radionuclides (e.g., ^{3}H and other volatile radionuclides; ^{55}Fe and other radionuclides that decay by electron capture).

Output: An initial list of radionuclides of potential concern including a brief narrative explaining why each radionuclide is on the list as well as an explanation of why certain radionuclides were considered but not listed. This list may be modified as more project-specific information becomes available. It is better to include radionuclides on the initial list even if the probability that they significantly contribute to the addressed concerns is small. The consequence of discovering an additional radionuclide of

concern late in a project generally outweighs the effort of evaluating its potential during planning.

3.3.2 Identify Concentration Ranges

Once the radionuclides of concern have been identified, the expected concentration range for each radionuclide should be determined. Historical data, process knowledge, previous studies, and preliminary survey or characterization results if available, can be used to determine the expected concentration range for each analyte. While most analytical protocols are applicable over a fairly large concentration range for the radionuclide of concern, performance over a required concentration range can serve as an MQO for the protocol-selection process, thereby eliminating any analytical protocols that cannot accommodate this need. In addition, knowledge of the expected concentration ranges for all of the radionuclides of concern can be used to identify possible chemical or spectral interferences that might lead to the elimination of some of the alternative analytical protocols.

Output: The expected concentration range for each radionuclide of concern and any constituent with the potential for causing chemical or radiological interference.

3.3.3 Identify and Characterize Matrices of Concern

During a directed project planning process, the matrices of concern should be identified clearly. Typical matrices may include surface soil, subsurface soil, sediment, surface water, groundwater, drinking water, air particulates, biota, structural materials, metals, etc. Historical data, process knowledge, previous studies, conceptual site models, transport models, and other such sources generally are used to identify matrices of concern. It is critical to be as specific as possible when identifying a matrix.

Information on the chemical and physical characteristics of a matrix is extremely useful. Therefore, in addition to identifying the matrices of concern, every effort should be made to obtain any information available on the chemical and physical characteristics of the matrices. This information is particularly important when determining the required specificity of the analytical protocol (i.e., the ability to accommodate possible interferences). It is also important to identify any possible hazards associated with the matrix, such as the presence of explosive or other highly reactive chemicals. Issues related to specific matrices, such as filtration of water samples and removal of foreign material, are discussed in more detail in Section 3.4 ("Matrix-Specific Analytical Planning Issues") and Section 6.5.1.1 ("Matrices").

Output: A list of the matrices of concern along with any information on their chemical and physical characteristics and on possible hazards associated with them. The list of matrices of concern and the analyte list often are developed concurrently. In some

cases, one analyst list is applicable to all the matrices of concern, and in other cases there are variations in the analyte list for each matrix.

3.3.4 Determine Relationships Among the Radionuclides of Concern

Known or expected relationships among radionuclides can be used to establish "alternate" radionuclides that may be easier and less costly to measure. In most cases, an "easy-to-measure" radionuclide is analyzed, and the result of this analysis is used to estimate the concentration of one or more radionuclides that may be difficult to measure or costly to analyze.

One of the best known and easiest relationships to establish is between a parent radionuclide and its associated progeny. Once equilibrium conditions have been established, the concentration of any member of the decay series can be used to estimate the concentration of any other member of the series (see Attachment 14A, "Radioactive Decay And Equilibrium"). For example, the thorium decay series contains 12 radionuclides. If each radionuclide in this series is analyzed separately, the analytical costs can be very high. However, if equilibrium conditions for the decay series have been established, a single analysis using gamma spectrometry may be adequate for quantifying all of the radionuclides in the series simultaneously.

Similarly, process knowledge can be used to predict relationships between radionuclides. For example, in a nuclear power reactor, steel may become irradiated, producing radioactive isotopes of the elements present in the steel. These isotopes often include ^{60}Co, ^{63}Ni, and ^{55}Fe. Cobalt-60 decays by emission of a beta particle and two high-energy gamma rays, which are easily measured using gamma spectrometry. Nickel-63 also decays by emission of a beta particle but has no associated gamma rays. Iron-55 decays by electron capture and has several associated X-rays with very low energies. Laboratory analysis of ^{63}Ni and ^{55}Fe typically is time-consuming and expensive. However, because all three radionuclides are produced by the same mechanism from the same source material, there is an expected relationship at a given time in their production cycle. Once the relationship between these radionuclides has been established, the ^{60}Co concentration can be used as an alternate radionuclide to estimate the concentration of ^{63}Ni and ^{55}Fe.

The uncertainty in the concentration ratio between radionuclide concentrations used in the alternate analyte approach should be included as part of the combined standard uncertainty of the analytical protocol in the measurement process. Propagation of uncertainties is discussed in Chapter 19, *Measurement Uncertainty*.

Output: A list of known or potential radionuclide relationships, based upon parent-progeny relationships, previous studies, or process knowledge. A preliminary study to determine the project-specific radionuclide relationships may be necessary, and additional measurements may be required to confirm the relationship used during the project. This information may be used to develop a revised analyte list.

3.3.5 Determine Available Project Resources and Deadlines

The available project resources can have a significant impact on the selection or development of analytical protocols, as well as the number and type of samples to be analyzed. In addition, project deadlines and, in particular, required analytical turnaround times (see Section 6.5.3, "Radiological Holding and Turnaround Times") can be important factors in the selection and development of analytical protocols for a particular project. During a directed planning process, radioanalytical specialists can provide valuable information on typical costs and turnaround times for various types of laboratory analyses.

Output: A statement of the required analytical turnaround times for the radionuclides of concern and the anticipated budget for the laboratory analysis of the samples.

3.3.6 Refine Analyte List and Matrix List

As additional information about a project is collected, radionuclides may be added to or removed from the analyte list. There may be one analyte list for all matrices or separate lists for each matrix. Developing an analyte list is an iterative process, however. The list should become more specific during the project planning process.

Radionuclides might be added to the analyte list when subsequent investigations indicate that additional radionuclides were involved in a specific project. In some cases, radionuclides may be removed from the analyte list. When there is significant uncertainty about the presence or absence of specific radionuclides, the most conservative approach is to leave them on the list even when there is only a small probability that they may be present. Subsequent investigations may determine if specific radionuclides are actually present and need to be considered as part of the project. For example, a research laboratory was licensed for a specific level of activity from all radionuclides with atomic numbers between 2 and 87. Even limiting the analyte list to radionuclides with a half-life greater than six months results in a list containing several dozen radionuclides. A study may be designed to identify the actual radionuclides of concern through the use of historical records and limited analyses to justify removing radionuclides from the analyte list.

Output: A revised analyte list. Radionuclides can always be added to or removed from the analyte list, but justification for adding or removing radionuclides should be included in the project documentation.

3.3.7 Method Performance Characteristics and Measurement Quality Objectives

The output of a directed planning process includes DQOs for a project (Section 2.6, "Results of the Directed Planning Process"). DQOs apply to all data collection activities associated with a project, including sampling and analysis. In particular, DQOs for data collection activities

describe the overall level of uncertainty that a decisionmaker is willing to accept for project results. This overall level of uncertainty is made up of uncertainties from sampling and analysis activities.

Because DQOs apply to both sampling and analysis activities, what are needed from an analytical perspective are performance objectives specifically for the analytical process of a particular project. MARLAP refers to these performance objectives as MQOs. The MQOs can be viewed as the analytical portion of the overall project DQOs. In a performance-based approach, the MQOs are used initially for the selection and evaluation of analytical protocols and are subsequently used for the ongoing and final evaluation of the analytical data.

In MARLAP, the development of MQOs for a project depends on the selection of an action level and gray region for each analyte during the directed planning process. The term "action level" is used to denote the numerical value that will cause the decisionmaker to choose one of the alternative actions. The "gray region" is a set of concentrations close to the action level where the project planning team is willing to tolerate a relatively high decision error rate (see Chapter 2 and Appendices B and C for a more detailed discussion of action levels and gray region). MARLAP recommends that an action level and gray region be established for each analyte during the directed planning process.

MARLAP provides guidance on developing MQOs for select method performance characteristics such as:

- The method uncertainty at a specified concentration (expressed as an estimated standard deviation);
- The method's detection capability (expressed as the minimum detectable concentration, or MDC);
- The method's quantification capability (expressed as the minimum quantifiable concentration, or MQC);
- The method's range, which defines the method's ability to measure the analyte of concern over some specified range of concentration;
- The method's specificity, which refers to the ability of the method to measure the analyte of concern in the presence of interferences; and
- The method's ruggedness, which refers to the relative stability of method performance for small variations in method parameter values.

An MQO is a quantitative or qualitative statement of a performance objective or requirement for a particular method performance characteristic. An example MQO for the method uncertainty at a specified concentration, such as the action level, would be: "A method uncertainty of 0.01 Bq/g or less is required at the action level of 0.1 Bq/g." A qualitative example of an MQO for method specificity would be "The method must be able to quantify the amount of ^{226}Ra present, given elevated levels of ^{235}U in the samples."

The list provided in this section is not intended to be an exhaustive list of method performance characteristics, and for a particular project, other method performance characteristics may be important and should be addressed during the project planning process. In addition, one or more of the method performance characteristics listed may not be important for a particular project. From an analytical perspective, a key activity during project planning is the identification of important method performance characteristics and the development of MQOs for them.

In addition to developing MQOs for method performance characteristics, MQOs may be established for other parameters, such as data quality indicators (DQIs). DQIs are qualitative and quantitative descriptors used in interpreting the degree of acceptability or utility of data. The principal DQIs are precision, bias, representativeness, comparability, and completeness. These five DQIs are also referred to by the acronym PARCC; the "A" stands for "accuracy" instead of bias, although both indicators are included in discussions of the PARCC parameters (EPA, 2002). Because the distinction between imprecision and bias depends on context, and because a reliable estimate of bias requires a data set that includes many measurements, MARLAP focuses on developing an MQO for method uncertainty. Method uncertainty effectively combines imprecision and bias into a single parameter whose interpretation does not depend on context. This approach assumes that all potential sources of bias present in the analytical process have been considered in the estimation of the measurement uncertainty and, if not, that any appreciable bias would only be detected after a number of measurements of QC and performance-testing samples have been performed. MARLAP provides guidance on the detection of bias, for example, during analytical method validation and evaluation (Chapters 6, *Selection and Application of an Analytical Method*, and 7, *Evaluating Methods and Laboratories*).

While MARLAP does not provide specific guidance on developing MQOs for the DQIs, establishing MQOs for the DQIs may be important for some projects. EPA (2002) contains more information on DQIs. MARLAP provides guidance on developing MQOs for method performance characteristics in the next section.

3.3.7.1 Develop MQOs for Select Method Performance Characteristics

Once the important method performance characteristics for an analytical process have been identified, the next step is to develop MQOs for them. This section provides guidance on developing MQOs for the method performance characteristics listed in the previous section. As noted, other method performance characteristics may be important for a particular analytical process, and

MQOs should be developed for them during project planning. Many of these issues are discussed in Section 6.5 from the laboratory's perspective.

METHOD UNCERTAINTY

While measurement uncertainty is a parameter associated with an individual result and is calculated after a measurement is performed, MARLAP uses the term "method uncertainty" to refer to the predicted uncertainty of a measured value that would likely result from the analysis of a sample at a specified analyte concentration (see Attachment 3A for a general overview of the concept of measurement uncertainty). Method uncertainty is a method performance characteristic much like the detection capability of a method. Reasonable values for both characteristics can be predicted for a particular method based on typical values for certain parameters and on information and assumptions about the samples to be analyzed. These predicted values can be used in the method selection process to identify the most appropriate method based on a project's data requirements. Because of its importance in the selection and evaluation of analytical protocols and its importance in the evaluation of analytical data, MARLAP recommends that the method uncertainty at a specified concentration (typically the action level) always be identified as an important method performance characteristic, and that an MQO be established for it for each analyte/matrix combination.

The MQO for the method uncertainty at a specified concentration plays a key role in MARLAP's performance-based approach. It effectively links the three phases of the data life cycle: planning, implementation, and assessment. This MQO, developed during the planning phase, is used initially in the selection and validation of an analytical method for a project (Chapter 6). This MQO provides criteria for the evaluation of QC samples during the implementation phase (Appendix C, *MQOs for Method Uncertainty and Detection and Quantification Capability*, and Chapter 7, *Evaluating Methods and Laboratories*). It also provides criteria for verification and validation during the assessment phase (Chapter 8, *Radiochemical Data Verification and Validation*). The use of the project-specific MQOs for the method uncertainty of each analyte in the three phases of the life of a project, as opposed to arbitrary non-project-specific criteria, helps to ensure the generation of radioanalytical data of known quality appropriate for its intended use.

The MQO for method uncertainty for an analyte at a specified concentration, normally the action level, is related to the width of the gray region. The gray region has an upper bound and a lower bound. The upper bound typically is the action level. The width of the gray region is represented by the symbol Δ (delta). Given the importance of the gray region in establishing MQOs, the reader is strongly encouraged to review Section B3.7 in Appendix B and Attachment B-1 of Appendix B, which provide detailed guidance on setting up a gray region.

Appendix C provides the rationale and detailed guidance on the development of MQOs for method uncertainty. Outlined below is MARLAP's recommended guideline for developing MQOs for method uncertainty when a decision is to be made about the mean of a population

represented by multiple samples. Appendix C provides additional guidelines for developing MQOs for method uncertainty when decisions are to be made about individual items or samples.

If decisions are to be made about the mean of a sampled population, MARLAP recommends that the method uncertainty (u_{MR}) be less than or equal to the width of the gray region divided by 10 for sample concentrations at the upper bound of the gray region (typically the action level). If this method uncertainty cannot be achieved, the project planners should require at least that the method uncertainty be less than or equal to the width of the gray region divided by 3 (Appendix C).

EXAMPLE

Suppose the action level is 0.1 Bq/g and the lower bound of the gray region is 0.02 Bq/g. If decisions are to be made about survey units based on samples, then the required method uncertainty (u_{MR}) at 0.1 Bq/g is

$$\frac{\Delta}{10} = \frac{0.1 - 0.02}{10} = 0.008 \text{ Bq/g}$$

If this uncertainty cannot be achieved, then a method uncertainty (u_{MR}) as large as $\Delta / 3 =$ 0.027 Bq/g may be allowed if more samples are taken.

In the example above, the required method uncertainty (u_{MR}) is 0.008 Bq/g. In terms of method selection, this particular MQO calls for a method that can ordinarily produce measured results with expected combined standard uncertainties (1σ) of 0.008 Bq/g or less at sample concentrations at the action level (0.1 Bq/g in this example). Although individual measurement uncertainties will vary from one measured result to another, the required method uncertainty is effectively a target value for the individual measurement uncertainties.

Output: MQOs expressed as the required method uncertainty at a specified concentration for each analyte.

DETECTION AND QUANTIFICATION CAPABILITY

For a particular project, the detection capability or the quantification capability may be identified as an important method performance characteristic during project planning (see Attachment 3B of this chapter and Attachment B-2 of Appendix B for a general overview of the concept of detection of an analyte). If the issue is whether an analyte is present in an individual sample and it is therefore important that the method be able to reliably distinguish small amounts of the analyte from zero, then an MQO for the detection capability should be established during project planning. If the emphasis is on being able to make precise measurements of the analyte

concentration for comparing the mean of a sampled population to the action level, then an MQO for the quantification capability should be established during project planning.

Detection Capability

When decisions are to be made about *individual items or samples* (e.g., drinking water samples), and the lower bound of the gray region is zero for the analyte of concern, the detection capability of the method is an important method performance characteristic, and an MQO should be developed for it. MARLAP recommends that the MQO for the detection capability be expressed as a required MDC (Chapter 20, *Detection and Quantification Capabilities*).

Outlined below is MARLAP's recommended guideline for developing MQOs for detection capability. Appendix C provides the rationale along with detailed guidance on the development of MQOs for detection capability.

If the lower bound of the gray region is zero, and decisions are to be made about individual items or specimens, choose an analytical method whose MDC is no greater than the action level.

Quantification Capability

When decisions are to be made about a *sampled population* and the lower bound of the gray region is zero for the analyte of concern, the quantification capability of the method is an important method performance characteristic and an MQO should be developed for it. MARLAP recommends that the MQO for the quantification capability be expressed as a required MQC (Chapter 20).

Outlined below is MARLAP's recommended guideline for developing MQOs for quantification capability. The MQC, as used in the guideline, is defined as the analyte concentration at which the relative standard uncertainty is 10 percent (see Chapter 19). Appendix C provides the rationale along with detailed guidance on the development of MQOs for quantification capability.

If the lower bound of the gray region is zero, and decisions are to be made about a sampled population, choose an analytical method whose MQC is no greater than the action level.

If an MQO for method uncertainty has been established, then establishing an MQO for the quantification capability in terms of a required MQC is somewhat redundant because an MQC is defined in terms of a specified relative standard uncertainty. However, this method performance characteristic is included in MARLAP for several reasons. First, it has been included to emphasize the importance of the quantification capability of a method for those instances where the issue is not whether an analyte is present or not—for example measuring ^{238}U in soil where the presence of the analyte is given—but rather how precisely the analyte can be measured. Second, this method performance characteristic has been included so as to promote the MQC as an

important method parameter. And last, it has been included as an alternative to the overemphasis on establishing required detection limits in those instances where detection (reliably distinguishing an analyte concentration from zero) is not the key analytical question.

Output: MQOs for each analyte should be expressed as (a) *MQCs* if the lower bound of the gray region is zero and decisions are to be made about a sample population or (b) *MDCs* if the lower bound of the gray region is zero, and decisions are to be made about individual items or samples.

RANGE

Depending on the expected concentration range for an analyte (Section 3.3.2), the method's range may be an important method performance characteristic. Most radioanalytical methods are capable of performing over a fairly large range of analyte concentrations. However, if the expected concentration range is large for an analyte, the method's range should be identified as an important method performance characteristic and an MQO should be developed for it. The radioanalytical specialist on the project planning team will determine when the expected concentration range of an analyte warrants the development of an MQO for the method's range. Because the expected concentration range for an analyte is based on past data, which may or may not be accurate, the MQO for the method's range should require that the method perform over a larger concentration range than the expected range. This precaution will help minimize the potential for selecting methods that cannot accommodate the actual concentration range of the analyte.

Output: MQOs for the method's concentration range for each analyte.

SPECIFICITY

Depending on the chemical and physical characteristics of the matrices, as well as the concentrations of analytes and other chemical constituents, the method's specificity may be an important method performance characteristic for an analytical process. Method specificity refers to the ability of the method to measure the analyte of concern in the presence of interferences. The importance of this characteristic is evaluated by the radioanalytical specialist based upon information about the expected concentration range of the analytes of concern, other chemical and radioactive constituents that may be present, and the chemical and physical characteristics of the matrices (Sections 3.3.2 and 3.3.3). If it is determined that method specificity is an important method performance characteristic, then an MQO should be developed for it. The MQO can be qualitative or quantitative in nature.

Output: MQOs for the method specificity for those analytes likely affected by interferences.

RUGGEDNESS

For a project that involves analyzing samples that are complex in terms of their chemical and physical characteristics, the method's ruggedness may be an important method performance characteristic. Method ruggedness refers to the relative stability of the method's performance when small variations in method parameter values are made, such as a change in pH, a change in amount of reagents used, etc. The importance of this characteristic is evaluated by the radioanalytical specialist based upon detailed information about the chemical and physical characteristics of the sample. If important, then an MOO should be developed for it, which may require performance data demonstrating the method's ruggedness for specified changes in select method parameters. Youden and Steiner (1975) and ASTM E1169 provide guidance on ruggedness testing.

Output: MQOs for method ruggedness for specified changes in select method parameters.

3.3.7.2 The Role of MQOs in the Protocol Selection and Evaluation Process

Once developed, the MQOs become an important part of the project's APSs and are subsequently incorporated into project plan documents (Chapter 4) and into the analytical Statement of Work (Chapter 5). In MARLAP, MQOs are used initially in the selection, validation, and evaluation of analytical protocols (Chapters 6 and 7). In a performance-based approach, analytical protocols are either accepted or rejected largely on their ability or inability to meet the project MQOs.

3.3.7.3 The Role of MQOs in the Project's Data Evaluation Process

Once the analytical protocols have been selected and implemented, the MQOs and—in particular—the MQOs for method uncertainty, are used in the evaluation of the resulting laboratory data relative to the project's analytical requirements. The most important MQO for data evaluation is the one for method uncertainty at a specified concentration. It is expressed as the required method uncertainty (u_{MR}) at some concentration, normally the action level (for this discussion, it is assumed that the action level is the upper bound of the gray region). When the analyte concentration of a laboratory sample is less than the action level, the combined standard uncertainty of the measured result should not exceed the required method uncertainty.

For example, if the required method uncertainty is 0.01 Bq/g or less at an action level of 0.1 Bq/g, then for any measured result less than 0.1 Bq/g, the laboratory's reported combined standard uncertainty should be less than or equal to 0.01 Bq/g. When the concentration is greater than the action level, the combined standard uncertainty of the measured result should not exceed the relative value of the required method uncertainty. If the required method standard uncertainty is 0.01 Bq/g or less at an action level of 0.1 Bq/g (10 percent of the action level), then for any measured result greater than 0.1 Bq/g, the laboratory's reported combined standard uncertainty should be no greater than 10 percent of the measured result. If an expanded uncertainty is

reported with each measured value, and the coverage factor also is specified (see Section 19.3.6, "Expanded Uncertainty"), the combined standard uncertainty may be calculated and checked against the required value. The check described relies on the laboratory's estimate of its measurement uncertainty. Additional checks are needed to ensure that the uncertainties are not seriously underestimated.

Appendix C provides guidance on developing criteria for QC samples based on the MQO for method uncertainty. Specifically, Appendix C contains equations for determining warning and control limits for QC sample results based on the project's MQO for method uncertainty.

The following example illustrates the use of the MQO for method uncertainty in evaluating QC sample results. Chapter 8, *Data Verification and Validation,* provides guidance on developing validation criteria based on the MQO for the required method uncertainty.

EXAMPLE

Suppose the upper bound of the gray region (the action level) is 0.1 Bq/g, and the required method uncertainty (u_{MR}) at this concentration is 0.01 Bq/g, or 10 percent. A routine laboratory control sample (LCS) is prepared with an analyte concentration of 0.150 Bq/g. (For the purpose of this example the uncertainty in the spike concentration is assumed to be negligible.) The lab analyzes the LCS with a batch of samples and obtains the measured result 0.140 ± 0.008 Bq/g, where 0.008 Bq/g is the combined standard uncertainty (1σ).

Question: Is this LCS result acceptable?

Answer: The LCS result may be acceptable if it differs from the accepted true value by no more than three times the required method uncertainty at that concentration. In this example the required method uncertainty is 10 percent at 0.150 Bq/g. So, the LCS result is required to be within 30 percent of 0.150 Bq/g, or in the range 0.105–0.195 Bq/g. Because 0.140 Bq/g is clearly in the acceptance range, the data user considers the result acceptable. Note also that the laboratory's reported combined standard uncertainty is less than the required method uncertainty, as expected.

3.3.8 Determine Any Limitations on Analytical Options

With the outputs of the resolution of a number of key analytical planning issues, such as a refined analyte list, MQOs for the analyte list, known relationship between radionuclides of concern, a list of possible alternate analytes, required analytical turnaround times, the analytical budget, etc., the project planning team may choose to limit the analytical options normally available to the laboratory. This decision may be based on information obtained during project planning, such as the absence of equilibrium between the analyte and other radionuclides in its decay chain, the

presence of other radionuclides known to cause spectral interferences, the presence of the analyte in a refractory form, etc. However, in the absence of such considerations, the project planning should allow the laboratory the flexibility of selecting any analytical approach that meets the analytical requirements in the APSs.

The role of the radioanalytical specialist is critical in determining if any limitations on analytical options are necessary because of the many laboratory-related issues and factors involved (see Section 2.5, "Directed Planning Process and Role of the Radioanalytical Specialists"). For example, if several of the radionuclides of concern on the target analyte list are gamma-emitters, the radioanalytical specialist can determine if gamma spectrometry is an appropriate technique given the required MQOs, matrices of concern, possible spectral interferences, etc. The radioanalytical specialist may determine that not only is gamma spectrometry an appropriate technique for the gamma-emitting radionuclides of concern, but because there is evidence that equilibrium conditions are present, the results for gamma spectrometry can be used for other radionuclides of concern in the same decay chain as the gamma-emitting radionuclides. In other instances, such as the use of gamma spectrometry to quantify ^{226}Ra in the presence of elevated levels of ^{235}U, the radioanalytical specialist may determine that gamma spectrometry is not an appropriate analysis due to possible spectral interferences. The following sections provide a brief overview of some measurement options.

3.3.8.1 Gamma Spectrometry

In general, gamma spectrometry has many advantages over other choices. It is capable of identifying and quantifying a large number of radionuclides. In comparison with other analyses, it offers a fairly quick turnaround time, and because it is generally a nondestructive technique and limited sample manipulation is involved, it is relatively inexpensive, particularly compared to analyses that require sample dissolution and chemical separations. It also allows for the use of relatively large sample sizes, thereby reducing the measurement uncertainty associated with subsampling at the laboratory. However, given its many advantages, gamma spectrometry cannot be used to analyze for all radionuclides. For example, gamma spectrometry may not be able to achieve the project's MQOs, because some or all of the radionuclides of concern may not be gamma-emitters, interfering radionuclides may present problems, etc. The radioanalytical specialist on the planning team can evaluate the appropriateness of the use of gamma spectrometry for some or all of the radionuclides on the analyte list or for alternate analytes.

3.3.8.2 Gross Alpha and Beta Analyses

Gross alpha and gross beta analysis provides information on the overall level of alpha- and beta-emitting radionuclides present in a sample. The analysis has the advantage of a relatively quick turnaround time and generally is inexpensive compared to other analyses. The analysis also has significant limitations. It does not identify specific alpha- and beta-emitting radionuclides, so the source of the overall alpha and beta radiation is not determined by the analysis. It does not detect

contribution from low-energy beta-emitting radionuclides such as ^{3}H. Volatile radionuclides may be lost during analysis. The measurement uncertainty of the analysis, particularly for matrices other than water, tends to be larger than the measurement uncertainty of other analyses. However, even with these limitations, gross alpha and beta analysis can be an important and appropriate analysis for a project.

3.3.8.3 Radiochemical Nuclide-Specific Analysis

In many instances, due to the project's MQOs, the lack of an appropriate alternate analyte, the lack of equilibrium conditions, etc., radiochemical nuclide-specific analyses are required. This is often true when radionuclides such as ^{3}H, ^{14}C, ^{90}Sr, isotopes of Pu, ^{99}Tc, etc., are on the analyte list. These analyses generally involve more manipulation of the samples than do gamma spectrometry and gross alpha and beta analysis. These analyses often require sample dissolution and chemical separation of the radionuclides of concern. For liquid scintillation counting, distillation is usually required for water samples, and some oxidative/combustion procedure is usually required for solid samples. Because of this, these analyses generally have longer turnaround times and are more expensive than other analyses.

Given the many analytical factors and considerations involved, *the role of the radioanalytical specialist is critical to determining if any limitations on analysis options are necessary.*

Output: Any limitations on analysis options, if appropriate.

3.3.9 Determine Method Availability

After the required analyses have been specified along with their associated sample matrices, the required MQOs, the analytical turnaround times, etc., the radioanalytical specialist should be able to determine if there are analytical methods currently available to meet the project's requirements.

If there are no known analytical methods that would meet the project's analytical requirements, the project planning team must evaluate options. They may decide to reevaluate the analytical data requirements, such as the MQOs, to see if they can be changed to allow the use of existing methods or increase the analytical budget and project timeline to allow for method development.

Output: A statement of method availability.

3.3.10 Determine the Type and Frequency of, and Evaluation Criteria for, Quality Control Samples

There are three main categories of laboratory QC samples—blanks, replicates, and spikes. In addition, there are different types of blanks, replicates, and spikes. For example, spikes can be

matrix spikes, laboratory control samples, external performance evaluation samples, etc. Chapter 18 (*Laboratory Quality Control*) contains a detailed discussion of the different types of QC samples and the information they provide. Because the results of the three main types of QC samples often are used to evaluate different aspects of the analytical process, most projects should employ all three types as part of the QC process.

The frequency of laboratory QC sampling for a project essentially represents a compromise between the need to evaluate and control the analytical process and the resources available. In addition, the nature of the project and the intended use of the data will play a role in determining the frequency of QC samples required. For example, the frequency of QC samples for a project involving newly developed methods for analytes in a complex matrix normally should be greater than the frequency of QC samples for a project using more established methods on a simpler matrix, assuming the intended use of the data is the same for both projects. The radioanalytical specialists on the project planning team play a key role in determining the type and frequency of QC samples for a project.

In order to adequately evaluate laboratory data, it is important that the QC samples be clearly linked to a group of project samples. Typically, this is done by analyzing QC samples along with a batch of samples and reporting the results together (see Chapter 18).

In addition to determining the type and frequency of QC samples, evaluation criteria for the QC sample results should be developed during the directed planning process and incorporated into the project's APSs. Appendix C provides guidance on developing criteria for QC samples and contains equations that calculate warning and control limits for QC sample results based on the project's MQO for method uncertainty.

Output: List of type and frequency of QC samples required and the criteria for evaluating QC sample results.

3.3.11 Determine Sample Tracking and Custody Requirements

A procedural method for sample tracking should be in place for all projects so that the proper location and identification of samples is maintained throughout the life of the project. Sample tracking should cover the entire process from sample collection to sample disposal. For some projects, a chain-of-custody (COC) process is needed. COC procedures are particularly important in demonstrating sample control when litigation is involved. In many cases, federal, state, or local agencies may require that COC be maintained for specific samples. Chapter 11, *Sample Receipt, Inspection, and Tracking*, provides guidance on sample tracking and COC. It is important that the requirements for sample tracking be clearly established during project planning.

Output: Project sample tracking requirements.

3.3.12 Determine Data Reporting Requirements

The data reporting requirements should be established during project planning. This involves determining not only what is to be reported but also how it is to be reported. Consideration also should be given to which information should be archived to allow a complete evaluation of the data in the future. Items that are routinely reported are listed below. It should be noted that this is not a comprehensive list, and some projects may require the reporting of more items while other projects may require the reporting of fewer items:

- Field sample identification number
- Laboratory sample identification number
- Sample receipt date
- Analysis date
- Radionuclide
- Radionuclide concentration units
- Sample size (volume, mass)
- Aliquant size (volume, mass)
- Radionuclide concentration at specified date
- Combined standard uncertainty or expanded uncertainty (coverage factor should be indicated)
- Sample-specific minimum detectable concentration
- Analysis batch identification
- Quality control sample results
- Laboratory instrument identification
- Specific analytical parameters (e.g., chemical yields, counting times, etc.)
- Analytical method/procedure reference

It is important that the required units for reporting specific items be determined during project planning. MARLAP recommends that units of the International System of Units (SI) be used whenever possible. However, because regulatory compliance levels are usually quoted in traditional radiation units, it may be appropriate to report in both SI and traditional units, with one being placed in parentheses. *MARLAP also recommends that all measurement results be reported directly as obtained, including negative values, along with the measurement uncertainty—for example 2σ, 3σ, etc*. This recommendation addresses the laboratory's reporting of data to the project planning team or project manager; additional consideration should be given to how data will be reported to the general public. Additional guidance on data reporting, including a discussion of electronic data deliverables, is provided in Chapter 16, *Data Acquisition, Reduction, and Reporting for Nuclear Counting Instrumentation,* and in Chapter 5, *Obtaining Laboratory Services*.

Output: Data reporting requirements for a project.

3.4 Matrix-Specific Analytical Planning Issues

This section discusses a number of matrix-specific analytical planning issues common to many types of projects. For each matrix there is a discussion of several potential key analytical planning issues specific to that matrix. It should be noted that what may be a key analytical planning issue for one project, may not be a key issue for another project. The list of potential matrix-specific key analytical planning issues discussed in this section is summarized in Table 3.1. Table 3.1 is not a comprehensive list, but rather is an overview of some common matrix-specific planning issues. Parenthetical references associated with "potential key issues" in the table identify Part II chapters where these issues are discussed in detail.

This section is divided into solids, liquids, filters and wipes. While filters and wipes are solids, they are discussed separately because of the unique concerns associated with them.

TABLE 3.1 — Common matrix-specific analytical planning issues

MATRIX	RECOMMENDED KEY ISSUES	POTENTIAL KEY ISSUES (Reference Chapters)
Solids (soil, sediment, structural material, biota, metal, etc.)	Homogenization Subsampling Removal of unwanted material	Container type (Chapter 10) Container material (10) Sample preservation (10) Surveying samples for health and safety (11) Volatile compounds (10) Sample identification (10, 11, 12) Cross-contamination (10) Sample size (10, 11, 12) Compliance with radioactive materials license (11) Compliance with shipping regulations (11) Chemical and physical form of the substrate (13, 14)
Liquids (drinking water, groundwater, precipitation, solvents, oils, etc.)	Is filtering required? Sample preservation Should sample be filtered or preserved first?	Sample identification (Chapters 10, 11, 12) Volume of sample (10) Immiscible layers (12) Precipitation (12) Total dissolved solids (12) Reagent background (12) Compliance with radioactive materials license (11) Compliance with shipping regulations (11)
Filters and Wipes	Filter material Pore size Sample volume or area wiped	Sample identification (Chapters 10, 11, 12) Compliance with radioactive materials license (11) Compliance with shipping regulations (11) Subsampling (12) Background from filter material (12)

3.4.1 Solids

Solid samples consist of a wide variety of materials that include soil and sediment, plant and animal tissue, concrete, asphalt; trash, etc. In general, most solid samples do not require preservation (Chapter 10) but do require specific processing both in the field and in the laboratory. In certain instances, some biota samples may require preservation, primarily in the form of lowered temperatures, to prevent sample degradation and loss of water. Some common analytical planning issues for solid samples include the removal of unwanted materials (Section 3.4.1.1), homogenization and subsampling (Section 3.4.1.2), and sample dissolution (Section 3.4.1.3) For certain types of biological samples, removal and analysis of edible portions may be a key analytical planning issue.

3.4.1.1 Removal of Unwanted Materials

When a solid sample is collected in the field, extraneous material may be collected along with the "intended" sample. For example, when collecting a soil sample, rocks, plant matter, debris, etc., may also be collected. Unless instructed otherwise, samples received by the laboratory typically are analyzed exactly as they are received. Therefore, it is important to develop requirements regarding the treatment of extraneous materials. Ultimately, these guidelines should be based on the project's DQOs. The requirements should clearly state what, if anything, is to be removed from the sample and should indicate what is to be done with the removed materials. The guidelines should indicate where the removal process should occur (in the field, in the laboratory or at both locations) and the material to be removed should be clearly identified.

For soil samples, this may involve identifying rock fragments of a certain sieve size, plant matter, debris, etc., as extraneous material to be removed, weighed, and stored at the laboratory. If material is removed from a soil sample, consideration should be given to documenting the nature and weight of the material removed. For sediment samples, requirements for occluded water should be developed. In the case of biological samples, if the entire sample is not to be analyzed, the analytical portion should be identified clearly.

3.4.1.2 Homogenization and Subsampling

For many types of analyses, a portion of the sample sent to the laboratory must be removed for analysis. As with sampling in the field, this portion of the sample should be representative of the entire sample. Adequate homogenization and proper subsampling techniques are critical to obtaining a representative portion of the sample for analysis. Developing requirements for—and measuring the adequacy of—homogenization processes and subsampling techniques can be complicated for various types of solid matrices. General guidance on homogenization and subsampling is provided in Chapter 12 and Appendix F. The input of the radioanalytical specialist as a member of the project planning team is critical to developing requirements for homogenization processes and subsampling techniques.

3.4.1.3 Sample Dissolution

For many analyses, a portion of the solid sample must undergo dissolution before the analyte of interest can be measured. The decision as to which technique to employ for sample dissolution is best left to the laboratory performing the analysis. The radioanalytical specialist can review any information on the chemical and physical characteristics of the matrices of concern and incorporate any relevant information into the APSs.

3.4.2 Liquids

Liquids include aqueous liquids (e.g., surface water, groundwater, drinking water, aqueous process wastes, and effluents), nonaqueous liquids (e.g., oil, solvents, organic liquid process wastes), and mixtures of aqueous and nonaqueous liquids.

A key analytical planning issue for most liquids is whether or not filtering is required or necessary (Section 10.3.2). The question of whether or not to filter a liquid is generally defined by the fundamental analytical question. If the question is related to total exposure from ingestion, the liquids are generally not filtered or the filters are analyzed separately and the results summed. If the question is concerned with mobility of the analyte the concentration in the liquid fraction becomes more important than the concentration in the suspended solids (although some suspended solids may still be important to questions concerning mobility of contamination). In many projects, all of the liquids are filtered and the question becomes which filters need to be analyzed. Issues related to this decision include where and when to filter (Chapter 10); homogenization and subsampling (Chapter 10); volatile compounds (Chapter 10); screening for health and safety (Chapter 11); and cross-contamination (Chapter 10).

Another key analytical planning issue involves preservation of liquid samples, which is also discussed in Chapter 10. Sample preservation involves decisions about the method of preservation (temperature or chemical, Chapter 10), container type and material (Chapter 10), and chemical composition of the sample (Chapters 13 and 14). Preservation of radionuclides in liquids is generally accomplished in the same manner as preservation of metals for chemical analysis. There are of course exceptions such as for ^{3}H and ^{129}I.

A third key analytical issue results from the first two issues and involves the decision of which issue should be resolved first. Should the sample be filtered and then preserved, or preserved first and filtered later? This issue is also discussed in Chapter 10. In general, acid is used to preserve liquid samples. Because acid brings many radionuclides into solution from suspended or undissolved material, filtering is generally performed in the field prior to preserving the sample with acid.

3.4.3 Filters and Wipes

Filters include a wide variety of samples, including liquid filters, air filters for suspended particulates, and air filters for specific compounds. Once the decision to filter has been made, there are at least three key analytical planning issues: filter material, effective pore size, and volume of material to be filtered.

The selection of filter or wipe material can be very important. The wrong filter or wipe can dissolve, break, clog, or tear during sample collection or processing, thus invalidating the sample. Chapter 10 includes a discussion of the various types of filter and wipe materials. Issues influencing this decision include the volume of material to be filtered, the loading expected on the filter, and the chemical composition of the material to be filtered.

The volume of material to be filtered, or area to be wiped, is generally determined by the detection requirements for the project. Lower detection limits require larger samples. Larger samples may, in turn, result in problems with shipping samples or analytical problems where multiple filters were required to meet the requested detection limits.

3.5 Assembling the Analytical Protocol Specifications

After key general and matrix-specific analytical planning issues have been identified and resolved, the next task of the project planning team is to organize and consolidate the results of this process into APSs for the project. In general, there will be an APS for each type of analysis (analyte-matrix combination). At a minimum, the APS should include the analyte list, the sample matrix, possible interferences, the MQOs, any limitations on analysis options, the type and frequency of QC samples along with acceptance criteria, and any analytical process requirements (e.g., sample tracking requirements). The analytical process requirements should be limited to only those requirements that are considered essential to meeting the project's analytical data requirements. For example, if the analyte of concern is known to exist in a refractory form in the samples, then fusion for sample digestion may be included as an analytical process requirement. However, in a performance-based approach, it is important that the *level of specificity in the APSs should be limited to those requirements that are considered essential to meeting the project's analytical data requirements*. The APS should be a one- or two-page form that summarizes the resolution of key analytical planning issues.

Figure 3.2 provides an example form for APSs with references to sections in this chapter as major headers on the form. Figure 3.3 provides for the purpose of an example, an APS for ^{226}Ra in soil for an information gathering project.

3.6 Level of Protocol Performance Demonstration

As discussed in Section 3.3.7.3, during project planning, the project planning team should determine what level of analytical performance demonstration or method validation is appropriate for the project. The question to be answered is how the analytical protocols will be evaluated. There are three parts of this overall evaluation process: (1) the initial evaluation, (2) the ongoing evaluation, and (3) the final evaluation. This section briefly discusses the initial evaluation of protocol performance. Chapters 7 and 8 provide guidance on the ongoing and final evaluation of protocol performance, respectively.

The project planning team should determine what level of initial performance demonstration is required from the laboratory to demonstrate that the analytical protocols the laboratory proposes to use will meet the MQOs and other requirements in the APSs. The project planning team should decide the type and amount of performance data required. For example, for the analysis of ^{3}H in drinking water, the project planning team may decide that past performance data from the laboratory, such as the results of internal QC samples for the analysis of ^{3}H in drinking water, are sufficient for the initial demonstration of performance for the laboratory's analytical protocols if they demonstrate the protocol's ability to meet the MQOs. If the analysis is for ^{238}Pu in a sludge, the project planning team may decide that past performance data (if it exists) would not be sufficient for the initial demonstration of performance. The planning team may decide that satisfactory results on performance evaluation samples would be required for the initial demonstration of analytical protocol performance. Section 6.6 ("Method Validation") provides detailed guidance on protocol performance demonstration/method validation, including a tiered approach based on the project analytical needs and available resources.

3.7 Project Plan Documents

Once the APSs have been completed, they should be incorporated into the appropriate project plan documents and, ultimately, into the analytical Statement of Work. Chapters 4 and 5 provide guidance on the development of project plan documents and analytical Statements of Work, respectively. While the APSs are concise compilations of the analytical data requirements, the appropriate plan documents should detail the rationale behind the decisions made in the development of the APSs.

Analytical Protocol Specifications

Analyte List: (Section 3.3.1, 3.3.7) **Analysis Limitations**: (Sections 3.3.9)

Matrix: (Section 3.3.3) **Possible Interferences**: (Sections 3.3.2, 3.3.7)

Concentration Range: (Section 3.3.2) **Action Level**: (Section 3.3.7)

MQOs:

(Section 3.3.7) (Section 3.3.7)

(Section 3.3.7) (Section 3.3.7)

QC Samples		
Type	**Frequency**	**Evaluation Criteria**
(Section 3.3.10)	(Section 3.3.10)	(Section 3.3.10)
(Section 3.3.10)	(Section 3.3.10)	(Section 3.3.10)
(Section 3.3.10)	(Section 3.3.10)	(Section 3.3.10)
(Section 3.3.10)	(Section 3.3.10)	(Section 3.3.10)

Analytical Process Requirements*	
Activity	**Special Requirements**
Field Sample Preparation and Preservation	(Section 3.4)
Sample Receipt and Inspection	(Section 3.3.12)
Laboratory Sample Preparation	(Section 3.4)
Sample Dissolution	(Section 3.4)
Chemical Separations	(Section 3.4)
Preparing Sources for Counting	(Section 3.4)
Nuclear Counting	(Section 3.4)
Data Reduction and Reporting	(Section 3.3.12)
Sample Tracking Requirements	(Section 3.3.11)
Other	

*Consistent with a performance-based approach, analytical process requirements should be kept to a minimum, therefore none or N/A may be appropriate for many of the activities.

FIGURE 3.2 — Analytical protocol specifications

Analytical Protocol Specifications (Example)

Analyte List: ^{226}Ra

Analysis Limitations: Must perform direct measurement of analyte or analysis of progeny allowed if equilibrium established at laboratory

Matrix: Soil

Possible Interferences: Elevated levels of ^{235}U

Concentration Range: 0.01 to 1.50 Bq/g

Action Level: 0.5 Bq/g

MQOs:

A method uncertainty (u_{MR}) of 0.05 Bq/g or less at 0.5 Bq/g

QC Samples		
Type	**Frequency**	**Evaluation Criteria**
Method blank	1 per batch	See attachment B*
Duplicate	1 per batch	See attachment B*
Matrix Spike	1 per batch	See attachment B*

Analytical Process Requirements	
Activity	**Special Requirements**
Field Sample Preparation and Preservation	None
Sample Receipt and Inspection	None
Laboratory Sample Preparation	None
Sample Dissolution	None
Chemical Separations	None
Preparing Sources for Counting	None
Nuclear Counting	None
Data Reduction and Reporting	See Attachment A*
Sample Tracking Requirements	Chain-of-Custody
Other	

* Attachments A and B are not provided in this example

FIGURE 3.3 — Example analytical protocol specifications

3.8 Summary of Recommendations

- MARLAP recommends that any assumptions made during the resolution of key analytical planning issues are documented, and that these assumptions are incorporated into the appropriate narrative sections of project plan documents.

- MARLAP recommends that an action level and gray region be established for each analyte during the directed planning process.

- MARLAP recommends that the method uncertainty at a specified concentration (typically the action level) always be identified as an important method performance characteristic, and that an MQO be established for it for each analyte.

- MARLAP recommends that the MQO for the detection capability be expressed as a required minimum detectable concentration.

- MARLAP recommends that the MQO for the quantification capability be expressed as a required minimum quantifiable concentration.

- MARLAP recommends that if the lower bound of the gray region is zero, and decisions are to be made about individual items or specimens, an analytical method should be chosen whose MDC is no greater than the action level.

- MARLAP recommends that if the lower bound of the gray region is zero, and decisions are to be made about a sampled population, choose an analytical method whose MQC is no greater than the action level.

- MARLAP recommends that units of the International System of Units (SI) be used whenever possible.

- MARLAP recommends that all measurement results be reported directly as obtained, including negative values, along with the measurement uncertainty.

3.9 References

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ATTACHMENT 3A
Measurement Uncertainty

3A.1 Introduction

No measurement is perfect. If one measures the same quantity more than once, the result generally varies with each repetition of the measurement. Not all the results can be exactly correct. In fact it is generally the case that no result is exactly correct. Each result has an "error," which is the difference between the result and the true value of the measurand (the quantity being measured). Ideally, the error of a measurement should be small, but it is always present and its value is always unknown. (Given the result of a measurement, it is impossible to know the error of the result without knowing the true value of the measurand.)

Since there is an unknown *error* in the result of any measurement, the measurement always leaves one with some *uncertainty* about the value of the measurand. What is needed then is an estimate of the range of values that could reasonably be attributed to the measurand on the basis of the measurement. Determining such a range of reasonable values is the purpose of evaluating the numerical "uncertainty" of the measurement (ISO, 1993).

This attachment gives only a brief overview of the subject of measurement uncertainty. Chapter 19 (*Measurement Uncertainty*) of this manual describes the evaluation and expression of measurement uncertainty in more detail.

3A.2 Analogy: Political Polling

The uncertainty of a laboratory measurement is similar to the "margin of error" reported with the results of polls and other surveys. Note that a political poll is a form of measurement, the measurand in this case being the fraction of likely voters who support a specified candidate. (The fraction is usually reported as a percentage.) The margin of error for the poll result is a kind of measurement uncertainty.

Suppose a poll of 1200 people indicates that 43 percent of the population supports a particular candidate in an election, and the margin of error is reported to be 3 percent. Then if the polling procedure is unbiased, one can be reasonably confident (but not certain) that the actual percentage of people who support that candidate is really between 40 percent and 46 percent.

Political polling results can be wildly inaccurate, and the predicted winner sometimes loses. One reason for this problem is the difficulty of obtaining an unbiased sample of likely voters for the poll. A famous example of this difficulty occurred in the presidential election of 1936, when a polling organization chose its sample from a list of people who owned telephones and automobiles and predicted on the basis of the poll that Alf Landon would defeat Franklin Roosevelt. A

significant source of inaccuracy in the result was the fact that many voters during the Great Depression were not affluent enough to own telephones and automobiles, and those voters tended to support FDR, who won the election in a landslide. Another famous example of inaccurate polling occurred in the 1948 presidential election, when polls erroneously predicted that Thomas Dewey would defeat Harry Truman. It seems that the polls in this case were simply taken too early in the campaign. They estimated the fraction of people who supported Dewey at the time the polls were taken, but the fraction who supported him on election day was lower. So, the margin of error in each of these cases was not a good estimate of the total uncertainty of the polling result, because it did not take into account significant sources of inaccuracy. A more complete estimate of the uncertainty would have combined the margin of error with other uncertainty components associated with possible sampling bias or shifts in public opinion. Similar issues may arise when laboratories evaluate measurement uncertainties.

3A.3 Measurement Uncertainty

To obtain a single numerical parameter that describes the uncertainty of a measured result in the laboratory requires one to consider all the significant sources of inaccuracy. An internationally accepted approach to the expression of measurement uncertainty involves evaluating the uncertainty first in the form of an estimated standard deviation, called a *standard uncertainty* (ISO, 1995). A standard uncertainty is sometimes informally called a "one-sigma" uncertainty.

In the political polling example above, the measurand is the fraction, p, of likely voters who support candidate X. The poll is conducted by asking 1,200 likely voters whether they support candidate X, and counting the number of those who say they do. If m is the number who support X, then the pollster estimates p by the quotient m / 1200. Pollsters commonly evaluate the standard uncertainty of p as $u(p) = 1 / 2\sqrt{1200}$.

After the standard uncertainty of a result is calculated, finding a range of likely values for the measurand consists of constructing an interval about the result by adding and subtracting a multiple of the standard uncertainty from the measured result. Such a multiple of the uncertainty is called an *expanded uncertainty*. The factor, k, by which the standard uncertainty is multiplied is called a *coverage factor*. Typically the value of k is a small number, such as 2 or 3. If $k = 2$ or 3, the expanded uncertainty is sometimes informally called a "two-sigma" or "three-sigma" uncertainty. An expanded uncertainty based on a coverage factor of 2 provides an interval about the measured result that has a reasonably high probability of containing the true value of the measurand (often assumed to be about 95 percent), and an expanded uncertainty based on a coverage factor of 3 typically provides an interval with a very high probability of containing the true value (often assumed to be more than 99 percent).

In the polling example, the definition of the margin of error is equivalent to that of an expanded uncertainty based on a coverage factor of $k = 2$. Thus, the margin of error equals 2 times $u(p)$, or $1 / \sqrt{1200}$, which is approximately 3 percent.

3A.4 Sources of Measurement Uncertainty

In radiochemistry the most familiar source of measurement uncertainty is counting statistics. Mathematically, the uncertainty of a radiation measurement due to counting statistics is closely related to the uncertainty represented by the margin of error for a political poll. If one prepares a source from a measured amount of radioactive material, places the source in a radiation counter, and makes several 10-minute measurements, the number of counts observed will not always be the same. A typical set of five results might be as follows:

101, 115, 88, 111, 103

Similarly, if the political poll described above were repeated five times with different groups of likely voters, the number of respondents in each poll who indicate they support the specified candidate might be as follows:

523, 506, 520, 516, 508

In either case, whether the numbers come from radiation counting or political polling, there is some inherent variability in the results due to random sampling and counting. In radiation counting, the variability exists partly because of the inherently random nature of radioactive decay and partly because the radiation counter is not perfectly efficient at detecting the radiation emitted from the source. In political polling, the variability exists because only a fraction of voters support the candidate and only a limited number of voters are surveyed.

As noted above, there are other potential sources of uncertainty in a political poll. The difficulty in polling is in obtaining a representative sample of likely voters to be surveyed. A similar difficulty is generally present in radiochemical analysis, since many analytical methods require that only a small fraction of the entire laboratory sample be analyzed. The result obtained for that small fraction is used to estimate the concentration of analyte in the entire sample, which may be different if the fraction analyzed is not representative of the rest of the material.

There are many other potential sources of uncertainty in a radiochemical measurement, such as instrument calibration standards, variable background radiation (e.g., cosmic radiation), contaminants in chemical reagents, and even imperfect mathematical models. Some of these errors will vary randomly each time the measurement is performed, and are considered to be "random errors." Others will be fixed or may vary in a nonrandom manner, and are considered to be "systematic errors." However, the distinction between a random error and a systematic error is relatively unimportant when one wants to know the quality of the result of a single measurement.

Generally, the data user wants to know how close the result is to the true value and seldom cares whether the (unknown) error of the result would vary or remain fixed if the measurement were repeated. So, the accepted methods for evaluating and expressing the *uncertainty* of a measurement make no distinction between random and systematic errors. Components of the total uncertainty due to random effects and systematic effects are mathematically combined in a single uncertainty parameter.

3A.5 Uncertainty Propagation

In a radiochemical measurement one typically calculates the final result, y, called the "output estimate," from the observed values of a number of other variables, $x_1,x_2,...,x_N$, called "input estimates," using a mathematical model of the measurement. The input estimates might include quantities such as the gross sample count, blank count, count times, calibration factor, decay factors, aliquant size, chemical yield, and other variables. The standard uncertainty of y is calculated by combining the standard uncertainties of all these input estimates using a mathematical technique called "uncertainty propagation." The standard uncertainty of y calculated in this manner is called a "combined standard uncertainty" and is denoted by $u_c(y)$.

Radiochemists, like pollsters, have traditionally provided only partial estimates of their measurement uncertainties, because it is easy to evaluate and propagate radiation counting uncertainty — just as it is easy to calculate the margin of error for a political poll. In many cases the counting uncertainty is the largest contributor to the overall uncertainty of the final result, but in some cases other uncertainty components may dominate the counting uncertainty — just as the polling uncertainty due to nonrepresentative sampling may dominate the uncertainty calculated from the simple margin-of-error formula. MARLAP recommends (in Chapter 19) that all of the potentially significant components of uncertainty be evaluated and propagated to obtain the combined standard uncertainty of the final result.

3A.6 References

International Organization for Standardization (ISO). 1993. *International Vocabulary of Basic and General Terms in Metrology*. ISO, Geneva, Switzerland.

International Organization for Standardization (ISO). 1995. *Guide to the Expression of Uncertainty in Measurement*. ISO, Geneva, Switzerland.

ATTACHMENT 3B
Analyte Detection

3B.1 Introduction

In many cases one of the purposes of analyzing a laboratory sample is to determine whether the analyte is present in the sample.[1] If the data provide evidence that the analyte is present, the analyte is *detected*; otherwise, it is *not detected*. The purpose of this attachment is to explain the issues involved in analyte detection decisions, which are often misunderstood. More details are presented in Chapter 20 (*Detection and Quantification Capabilities*).

The result of a laboratory analysis is seldom if ever exactly equal to the true value of the measurand (the quantity being measured), because the result is affected by measurement error (see Attachment 3A). It is also rare for two or more analyses to produce exactly the same result, because some components of the measurement error vary randomly when a measurement is repeated. Typically some sources of error are well understood (e.g., radiation counting statistics) while others (e.g., reagent contamination and interferences) may or may not be. For these reasons, deciding whether an analyte is present in a sample is not always easy.

Acceptable methods for making detection decisions are based on statistical hypothesis testing. In any statistical hypothesis test there are two hypotheses, which are called the *null hypothesis* and the *alternative hypothesis*. Each hypothesis is a statement whose truth is unknown. Only one of the two hypotheses in a hypothesis test can be true in any given situation. The purpose of the test is to choose between the two statements. The null hypothesis is the statement that is presumed to be true unless there is adequate statistical evidence (e.g., analytical data) to the contrary. When the evidence for the alternative hypothesis is strong, the null hypothesis is rejected and the alternative hypothesis is accepted. When the evidence is weak, the null hypothesis is retained and thus must still be assumed to be true, or at least possibly true. In the context of analyte detection, the null hypothesis states that there is *no* analyte in the sample, while the alternative hypothesis states that there is *some* analyte in the sample.

The concept of a null hypothesis is similar to that of a presumption of innocence in a criminal trial, where the defendant is presumed to be innocent (the null hypothesis) unless there is strong legal evidence to the contrary. If the evidence is strong enough to meet the burden of proof, the defendant is found guilty (the alternative hypothesis). The important point here is that an acquit-

[1] In other cases, the analyte's presence in a sample may be known or assumed before the analysis. For example, project planners may want to know whether the concentration of a naturally occurring radionuclide, such as ^{238}U, in soil is above or below an action level, although there is little doubt that the analyte is present. In these cases it is usually not necessary to make a detection decision.

tal does not require proof of innocence—only a lack of proof of the defendant's guilt. Analogous rules apply in statistical hypothesis testing.

In the context of analyte detection, the null hypothesis states that there is no analyte in the sample; so, one must presume that no analyte is present unless there is sufficient analytical evidence to the contrary. Therefore, failing to detect an analyte is not the same thing as proving that no analyte is present. Generally, proving that there is no analyte in a sample is *impossible* because of measurement error. No matter how small the result of the measurement is, even if the result is zero or negative, one cannot be certain that there is not at least one atom or molecule of the analyte in the sample.

3B.2 The Critical Value

When a laboratory analyzes a sample, the measuring instrument produces a response, or gross signal, that is related to the quantity of analyte present in the sample, but random measurement errors cause this signal to vary somewhat if the measurement is repeated. A nonzero signal may be (and usually is) produced even when no analyte is present. For this reason the laboratory analyzes a blank (or an instrument background) to determine the signal observed when no analyte is present in the sample, and subtracts this blank signal from the gross signal to obtain the *net signal*. In fact, since the signal varies if the blank measurement is repeated, there is a blank signal *distribution*, whose parameters must be estimated. To determine how large the instrument signal for a sample must be to provide strong evidence for the presence of the analyte, one calculates a threshold value for the net signal, called the *critical value*, which is sometimes denoted by S_C. If the observed net signal for a sample exceeds the critical value, the analyte is considered "detected"; otherwise, it is "not detected."

Since the measurement process is statistical in nature, even when one analyzes an analyte-free sample, it is possible for the net signal to exceed the critical value, leading one to conclude incorrectly that the sample contains a positive amount of the analyte. Such an error is sometimes called a "false positive," although the term "Type I error" is favored by MARLAP. The probability of a Type I error is often denoted by α. Before calculating the critical value one must choose a value for α. The most commonly used value is 0.05, or 5 percent. If $\alpha = 0.05$, then one expects the net instrument signal to exceed the critical value in only about 5 percent of cases (one in twenty) when analyte-free samples are analyzed.

Figure 3B.1 depicts the theoretical distribution of the net instrument signal obtained when analyzing an analyte-free sample and shows how this distribution and the chosen Type I error probability, α, together determine the critical value of the net signal, S_C. The probability α is depicted as the area under the curve to the right of the dashed line. Note that decreasing the value of α, requires increasing the critical value (shifting the dashed line to the right), and increasing the value of α requires decreasing the critical value (shifting the dashed line to the left).

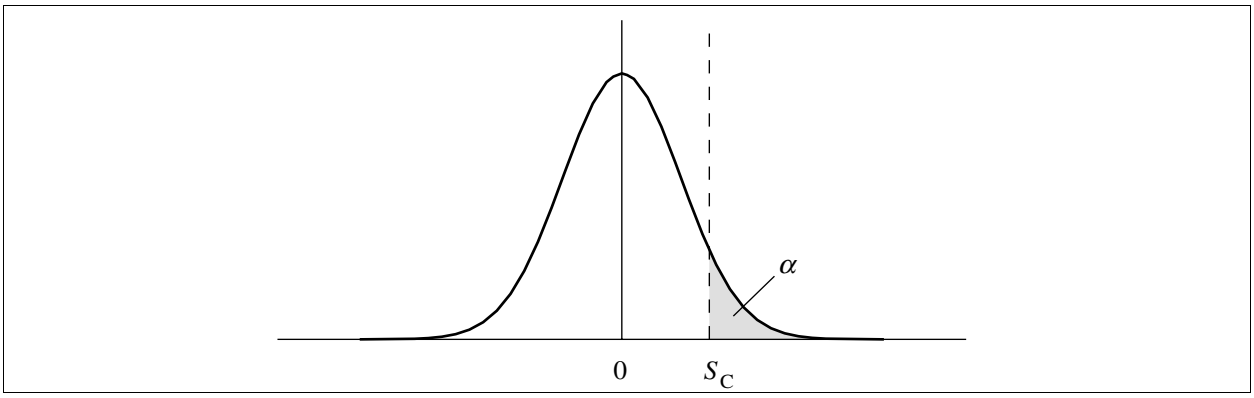

FIGURE 3B.1 — The critical value of the net signal

3B.3 The Minimum Detectable Value

As explained above, the critical value is chosen to limit the probability of a Type I decision error, which means incorrectly concluding that the analyte has been detected when it actually is not present. When the analyte actually *is* present in the sample being analyzed, another kind of decision error is possible: incorrectly failing to detect the analyte. The latter type of error is called a *Type II error*.

The *detection capability* of an analytical measurement process, or its ability to distinguish small positive amounts of analyte from zero, is defined in terms of the probability of a Type II error. The common measure of detection capability is the *minimum detectable value*, which equals the smallest true value (amount, activity, or concentration) of the analyte at which the probability of a Type II error does not exceed a specified value, β. [2] The definition of the minimum detectable value presumes that an appropriate detection criterion (i.e., the critical value) has already been chosen. So, the minimum detectable value is the smallest true value of the analyte that has a specified probability, $1 - \beta$, of generating an instrument signal greater than the critical value. The value of β, like that of α, is often chosen to be 0.05, or 5 percent. (See Figure 20.1 in Chapter 20 for a graphical illustration of the relationship between the critical value and the minimum detectable value.)

In radiochemistry, the minimum detectable value may be called the *minimum detectable concentration* (MDC), *minimum detectable amount* (MDA), or *minimum detectable activity* (also abbreviated as MDA). MARLAP generally uses the term "minimum detectable concentration," or MDC.

[2] Although the minimum detectable value is defined theoretically as a "true" value of the analyte, this value, like almost any true value in the laboratory, is not known exactly and can only be estimated. The important point to be made here is that the minimum detectable value should not be used as a detection threshold for the *measured value* of the analyte.

It is common in radiochemistry to report the MDC (or MDA) for the measurement process. Unfortunately, it is also common to use the MDC incorrectly as a critical value, which it is not. It is difficult to imagine a scenario in which any useful purpose is served by comparing a measured result to the MDC. Nevertheless such comparisons are used frequently by many laboratories and data validators to make analyte detection decisions, often at the specific request of project planners.

This common but incorrect practice of comparing the measured result to the MDC to make a detection decision produces the undesirable effect of making detection much harder than it should be, because the MDC is typically at least twice as large as the concentration that corresponds to the critical value of the instrument signal. In principle, a sample that contains an analyte concentration equal to the MDC should have a high probability (usually 95 percent) of producing a detectable result. However, when the MDC is used for the detection decision, the probability of detection is only about 50 percent, because the measured concentration is as likely to be below the MDC as above it. When an analyte-free sample is analyzed, the probability of a Type I error is expected to be low (usually 5 percent), but when the MDC is used for the detection decision, the probability of a Type I error is actually much smaller—perhaps 0.1 percent or less.

Sometimes it may be desirable to have a Type I error rate much less than 5 percent; however, this goal does not justify using the MDC for the detection decision. In this case, the correct approach is to specify the critical value based on a smaller value of α, such as 0.01 instead of 0.05.

MARLAP recommends that when a detection decision is required, the decision should be made by comparing the measured value (e.g., of the net instrument signal) to its critical value—not to the minimum detectable value.

3B.4 Sources of Confusion

There are several potential sources of confusion whenever one deals with the subject of analyte detection in radiochemistry. One source is the lack of standardization of terminology. For example, the term "detection limit" is used with different meanings by different people. In radiochemistry, the detection limit for a measurement process generally means the minimum detectable value. However, in other fields the term may correspond more closely to the critical value. In particular, in the context of hazardous chemical analysis, the term "method detection limit," which is abbreviated as MDL, is defined and correctly used as a critical value (i.e., detection threshold); so, the MDL is not a "detection limit" at all in the sense in which the latter term is commonly used in radiochemistry. Another potential source of confusion is the similarity between the abbreviations MDL and MDC, which represent very different concepts. Anyone who is familiar with only one of these terms is likely to be confused upon first encountering the other.

Another cause of confusion may be the practice of reporting undetectable results as "< MDC." If the measured result is less than the critical value, the practice of reporting "< MDC" may not be ideal, but at least it can be defended on the basis that when the measured value is less than the critical value, the true value is almost certainly less than the MDC. However, if this shorthand reporting format is not explained clearly, a reader may interpret "< MDC" to mean that the *measured* value was less than the MDC and for that reason was considered undetectable. The latter interpretation would be incorrect and might cause the reader to misunderstand the MDC concept. (MARLAP recommends in Chapter 19 that the laboratory always report the measured value and its uncertainty even if the result is considered undetectable.)

3B.5 Implementation Difficulties

Conceptually, the theory of detection decisions and detection limits is straightforward, but the implementation of the theory often presents difficulties. Such difficulties may include:

- Difficulty in preparing and measuring appropriate blanks,
- Variable instrument background,
- Sample-specific interferences, and
- Statistics of low-background radiation counting.

The concept of the "appropriate blank" is that of an artificial sample that is as much like a real sample as practical in all important respects, but which contains none of the analyte being measured. The most appropriate type of blank depends on the analyte and the measurement procedure.

Too often the critical value is based on the distribution of the instrument background, even when it is known that the presence of analyte in reagents and interferences from various sources cause the observed signal for an analyte-free sample to be somewhat elevated and more variable than the instrument background. This practice may produce a high percentage of Type I errors when the critical value is used as a detection threshold. In other cases, the instrument background measurement may overestimate the signal produced by an analyte-free sample and lead to higher Type II error rates. Note that the problem in either of these cases is not the use of the critical value but its incorrect calculation. There is still no justification for using the MDC as a detection threshold. Instead, the critical value should be based on a better evaluation of the distribution of the signal that is observed when analyte-free samples are analyzed.

Even when there are no interferences or reagent contamination, if the instrument background is variable, some of the commonly used expressions for the critical value (which are based on counting statistics only) may be inadequate. Again, the consequence of ignoring such variability when calculating the critical value may be a high percentage of Type I errors. In this case too, the mistake is not in how the critical value is used (as a detection threshold), but in how it is calculated.

A final issue to be discussed is how to calculate an appropriate critical value when the observed blank count is extremely low (e.g., less than 20 counts). Chapter 20 presents expressions for the critical value that should give good results (Type I error rates close to those expected) in these situations when the only variability is that due to counting statistics. However, when the blank count is low and there is additional variability, the usefulness of these expressions cannot be guaranteed, even when they are modified to account for the extra variability.