Multi-Agency Radiological Laboratory Analytical Protocols Manual

Part I Training
"The MARLAP Process"

United States Environmental Protection Agency, Region 9
and
California Department of Health Services
Sacramento, California
May 31–June 1, 2006

Multi-Agency Radiological Laboratory Analytical Protocols (MARLAP) Part I — "The MARLAP Process"

May 31, 2006

8:00	1 — Introduction	Bob Litman
8:30	2 — Directed Planning Process	Carl Gogolak
9:15	3 — Data Quality Objectives and the Gray Region*	Carl Gogolak
Noon	Lunch	
1:15	4 — Key Analytical Planning Issues*	Bob Litman
3:15	Break	
3:30	5 — Project Planning Documents	Dave McCurdy
3:50	6 — Measurement Uncertainty	Keith McCroan
4:45	Adjourn for the Day (Questions Welcome)	

June 1, 2006

8:00	7 — Evaluating Measurement Uncertainty*	Keith McCroan
9:30	8 — Obtaining Laboratory Services	Dave McCurdy
10:00	Break	
10:15	9 — Method Validation*	Dave McCurdy
12:15	Lunch	
1:30	10 — Evaluating Methods and Laboratories	Dave McCurdy
2:45	Break	
3:00	11 — Data Verification and Validation*	Bob Litman
4:45	Wrap Up and Adjourn (Questions Welcome)	

* With group exercise

Contents

Acronyms Used in the MARLAP Process

AL . . . . action level
APS . . . . Analytical Protocol Specification
COC . . . . chain of custody
CSU . . . . combined standard uncertainty
DL . . . . discrimination level
DQO . . . . data quality objective
GPC . . . . gas proportional counting
GUM . . . . . . *Guide to the Expression of Uncertainty in Measurement*
HSA . . . . historical site assessment
ISO . . . . International Organization for Standardization
LCS . . . . laboratory control sample
LGBR . . . . . . lower bound of the gray region
LSC . . . . liquid scintillation counting
MARLAP . . . *Multi-Agency Radiological Laboratory Analytical Protocols Manual*
MDA . . . . . . minimum detectable amount or minimum detectable activity
MDC . . . . . . minimum detectable concentration
MQC . . . . . . minimum quantifiable concentration
MQO . . . . . . measurement quality objective
MVRM . . . . . method validation reference material
QAPP . . . . . . quality assurance project plan
PE . . . . performance evaluation
PT . . . . performance/proficiency testing [materials]
PM . . . . project manager
RHT . . . . radiological holding time
ROI . . . . region of interest
RPD . . . . relative percent difference
SOW . . . . statement of work
SA . . . . spike concentration added
SR . . . . unspiked sample result
SSR . . . . spiked sample result
TAT . . . . turnaround time
TEC . . . . technical evaluation committee
UBGR . . . . . upper bound of the gray region
V&V . . . . verification and validation

Symbols Used in the MARLAP Process

σ The total standard deviation of the data. It is represented by:
$$\sigma = [\sigma_s^2 + \sigma_M^2]^{1/2}$$

σ_s The standard deviation of the contaminant concentration in the sampled population (i.e., the sampling contribution to uncertainty)

σ_M The "true" standard deviation of the measurement process (i.e., the laboratory contribution to uncertainty)

Δ The width of the gray region.
       Δ = (Action Level – Discrimination Level) = (AL–DL)
It also can be expressed as
       Δ = (upper bound of the gray region – lower bound of the gray region)

φ_{MR} Required *relative* method uncertainty above the action level (AL) expressed as a fraction:
$$\varphi_{MR} = [\, u_{MR} / AL]$$

u_{MR} Required *absolute* method uncertainty at and below the AL. An upper bound to the value of σ_M.
       $u_{MR} = \Delta/10$ for the mean of a sampled population
         $u_{MR} = \Delta/3$ for an individual sample

α The statistical factor for assessing the probability of an analyte being detected when none is present. Also referred to as the "Type I error rate." Commonly assigned a value of 0.05.

β The statistical factor for assessing the probability of an analyte <u>not</u> being detected when it <u>is</u> present. Also referred to as the "Type II error rate." Commonly assigned a value of 0.05.

Multi-Agency Radiological Analytical Protocols Manual (MARLAP)

1. Introduction

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Bob Litman — drbob20@comcast.net

Keith McCroan — mccroan.keith@epa.gov

Dave McCurdy — demccurdy@aol.com

Carl Gogolak, Ph.D., is a physicist with more than 35 years experience. He has conducted experimental and theoretical studies of low-level environmental radiation fields to assess the radiological impacts of energy production and to assure adequate environmental surveillance of nuclear facilities. He was a major contributor to both MARRSIM and MARLAP, for which he authored or co-authored several chapters and appendices dealing with uncertainty, the gray region, and data quality. He was an original developer and instructor on previous versions of the MARLAP Part I training course prior to his retirement from the Environmental Measurements Laboratory of the U.S. Department of Energy and later the Department of Homeland Security.

Robert Litman, Ph.D., has been a researcher and practitioner of nuclear and radiochemical analysis for the past 33 years. He is well respected in the nuclear power industry as a specialist in radiochemistry and instrumentation. Dr. Litman co-authored two chapters of MARLAP. His particular areas of expertise are gamma spectroscopy and radiochemical separations.

Keith McCroan, Ph.D., is an information technology specialist with the National Air and Radiation Environmental Laboratory of the U.S. Environmental Protection Agency, where he has worked since 1991. Although his formal education was in mathematics and computer science, he has become better known among radiochemists as a statistician and metrologist. Dr. McCroan was the principal author of five chapters and appendices of MARLAP, including the chapters on measurement uncertainty and detection and quantification limits, and was a contributor to four other chapters.

David E. McCurdy, Ph.D., is a nationally recognized expert in radioanalytical method development, and he has 39 years of experience in the areas of radiometrology, radiochemical method development, radiobioassay, radiological laboratory operations, environmental monitoring and pathway analysis. He was the principal author or co-author of seven chapters and appendices of MARLAP.

Contents

During the group exercises, you will follow the various steps needed to select and validate an analytical method for determining americium-241 in groundwater at a former nuclear extraction facility. Participants will form teams and apply MARLAP principles to:

- Determine the required method uncertainty at the action level

- Write an Analytical Protocol Specification for a selected nuclide/matrix combination

- Evaluate and approve a method based on laboratory validation documentation

- Apply data validation and verification qualifiers to a data set

- Perform representative uncertainty calculations

After this course, you will be able to —

1. Navigate through *MARLAP* and understand its organization

2. Recognize that the required method uncertainty is the key to the MARLAP process

3. Describe, using specific equations, how the required method uncertainty is used in the MARLAP process.

4. Apply the MARLAP process during the project planning, implementation, and assessment phases

- A multi-agency guidance manual for project planners and managers and radioanalytical laboratories

- Participants include: EPA, DOD, DOE, DHS, NRC, NIST, USGS, FDA, Kentucky, and California

- Companion to MARSSIM

Eight federal agencies (EPA, Defense, Energy, Homeland Security, Nuclear Regulatory Commission, Food and Drug Administration, US Geological Survey, National Institute of Standards and Technology) plus two states (Kentucky and California)

MARSSIM = *Multi-Agency Radiation Survey and Site Investigation Manual*. MARSSIM provides guidance on how to design and implement a study to demonstrate that a site meets appropriate release criteria.

MARLAP provides guidance and a framework for project planners and laboratory personnel to ensure that radioanalytical data will meet the needs of decisionmakers.

Websites:
MARLAP: http://www.epa.gov/radiation/marlap/
MARSSIM: http://www.epa.gov/radiation/marssim/

Provide guidance and a framework to assure that laboratory radioanalytical data meet a program's or project's specific needs and requirements

MARLAP Objectives

- Providing a framework and an information resource for using a performance-based approach for radioanalytical work
- Promoting a directed planning process involving radioanalytical laboratory expertise
- Providing guidance on how to link project planning, implementation and assessment from an analytical perspective
- Making collective knowledge and experience in radioanalytical laboratory work widely available
- Providing guidance on obtaining and evaluating laboratory services

MARLAP is not a methods manual.

Data Collection Activities

Examples of MARLAP's applicability —

- Cleanup of contaminated sites
- Environmental monitoring
- Waste management
- Effluent monitoring of licensed facilities
- Site characterization
- Emergency response
- Background studies
- Decommissioning of nuclear facilities

Manual Outline

MARLAP Part I (Volume 1)

- Chapter 1 — Introduction
- Chapter 2 — Project Planning Process
- Chapter 3 — Key Analytical Planning Issues and Developing APSs
- Chapter 4 — Project Plan Documents
- Chapter 5 — Obtaining Laboratory Services
- Chapter 6 — Selection and Application of an Analytical method
- Chapter 7 — Evaluating Methods and Laboratories
- Chapter 8 — Radiochemical Data Verification and Validation
- Chapter 9 — Data Quality Assessment
- Five Appendices

Part I principally directed towards the project planning, implementation and assessment phases and emphasizes:

- Preparation of project plan documents
- Establishing a Statement of Work (SOW)
- Identifying and obtaining proper laboratory services
- Performance-based method selection and approval
- Method validation guidance
- Initial and ongoing laboratory performance evaluation
- Data validation and assessment processes

Associated appendices cover:

A. Directed Planning Approaches
B. The DQO Process
C. MQOs for Method Uncertainty and Detection and Quantification Capability
D. Content of Project Plan Documents
E. Contracting Laboratory Services

While Part I is of greatest significance to project planners and managers, lab personnel need to understand what Part I contains in order to provide necessary input during the planning process.

This course concentrates on Part I.

Manual Outline (Continued)

MARLAP Part II (Volume 2)

- Chapter 10 — Field and Sampling Issues
- Chapter 11 — Sample Receipt, Inspection, and Tracking
- Chapter 12 — Laboratory Sample Preparation
- Chapter 13 — Sample Dissolution
- Chapter 14 — Separation Techniques
- Chapter 15 — Quantification of Radionuclides
- Chapter 16 — Data Acquisition, Reduction, and Reporting
- Chapter 17 — Waste Management
- Appendix F — Laboratory Subsampling

Part II directed towards laboratory personnel and the analysis process. Part II spans two printed volumes because of size

- Sample handling and preparation for analysis
- Techniques for sample dissolution
- Techniques for analyte separation
- Techniques for radiological counting of samples
- Data reduction
- Waste management in radioanalytical laboratories
- Quality control
- Statistical methods of data evaluation

MARLAP Part II (Volume 3)

- Chapter 18 — Laboratory Quality Control
- Chapter 19 — Measurement Uncertainty
- Chapter 20 — Detection and Quantification Capabilities
- Appendix G — Statistical Tables

- Planning phase
- Implementation phase
- Assessment phase
- Decision making

DATA LIFE CYCLE		
	PROCESS	PROCESS OUTPUTS
Planning	Directed Planning Process	Development of Data Quality Objectives and Measurement Quality Objectives (Including Optimized Sampling and Analytical Design)
Planning	Plan Documents	Project Plan Documents Including Quality Assurance Project Plan (QAPP); Work Plan or Sampling and Analysis Plan (SAP), Data Validation Plan, Data Quality Assessment Plan
Planning	Contracting Services	Statement of Work (SOW) and Other Contractual Documents
Implementation	Sampling	Laboratory Samples
Implementation	Analysis	Laboratory Analysis (Including Quality Control [QC] Samples) Complete Data Package
Assessment	Verification	Verified Data Data Verification Report
Assessment	Validation	Validated Data Data Validation Report
Assessment	Data Quality Assessment	Assessment Report
	Data of Known Quality Appropriate for the Intended Use	← → Decision

- Data life cycle provides structure for considering major project phases involving data collection
- Ensure that data will be of known quality and adequate to meet intended use
- Planning phase:
    - Directed planning process
    - Plan documents
    - Contracting services
- Implementation phase
    - Sampling
    - Analysis
- Assessment phase:
    - Verification
    - Validation
    - Data quality assessment

The MARLAP Process
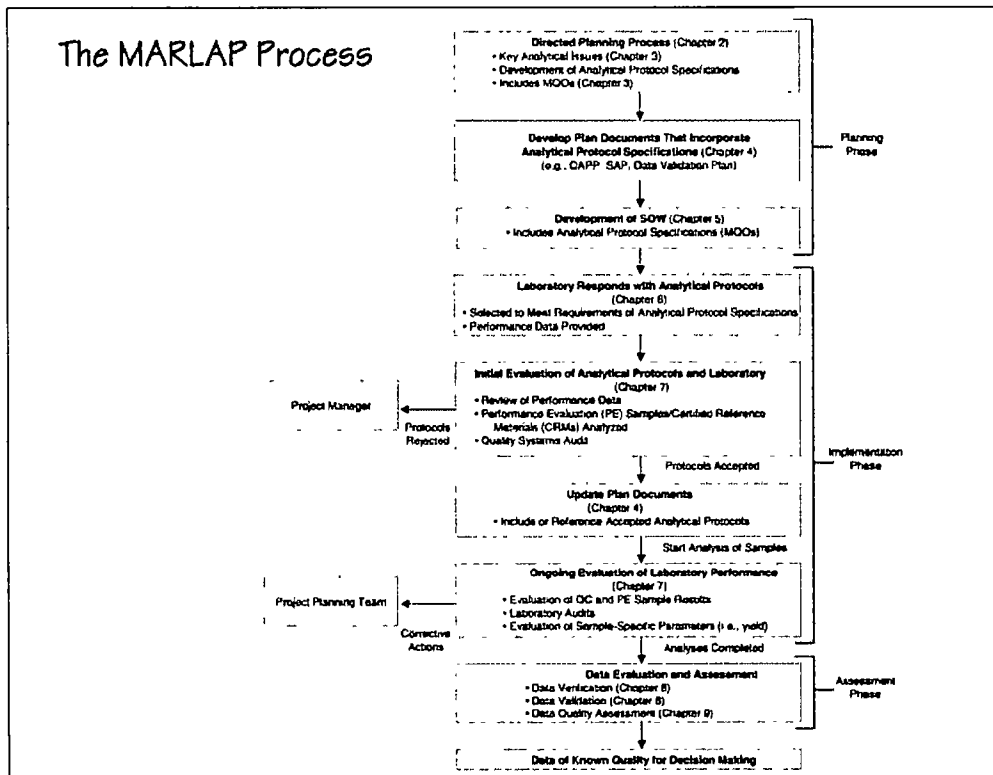
- MARLAP is an iterative process, with feedback.
- MARLAP establishes proper linkages among the three phases of the data life cycle.
- Integration of the phases ensures that the analytical data requirements (defined during planning) can serve as <u>measurement performance criteria</u> during implementation phase, and subsequently as <u>data evaluation criteria</u> during assessment phase.

Class Exercises

- Example: ^{90}Sr in milk (Instructors)
  - A MARLAP project example running through all the course modules
- Exercise: ^{241}Am in ground water (Participants)
  - Participants group into project teams and apply MARLAP principles applicable to each module
  - Information developed during each module will be used in subsequent exercises
- These exercises will demonstrate the MARLAP process and enhance your ability to use it on your own projects

Participant groups will work on exercises during:
- Module 3 — Data Quality Objectives and the Gray Region (Day 1)
- Module 4 — Key Analytical Planning Issues (Day 1)
- Module 7 — Evaluating Measurement Uncertainty (Day 2)
- Module 9 — Method Validation (Day 2)
- Module 11 — Data Validation and Verification (Day 2)

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- Focus on the planning phase of the project
- Provide a template for getting started
- Require teamwork in implementing the MARLAP process
- Meet the time available, but realistic

1. Introduction   13

The exercise will require participants to apply the MARLAP process by referring to materials located following Tabs 17 to 21 in the course book. These materials will be introduced by instructors at the appropriate time. Solutions will be distributed and discussed after each exercise.

- Delineating the gray region and determining the required method uncertainty (Module 3)
- Developing Analytical Protocol Specifications (Module 4)
- Determining measurement uncertainty (Module 7)
- Validating laboratory methods (Module 9)
- Data validation and verification (Module 10)

PROJECT PLANNING PROCESS

Module 2

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- How much data do we need?
- What will we measure?
- Where?
- How?

- *How will we know when to stop collecting data and make a decision?*

No Planning

- We will measure everything everywhere with the highest possible precision and accuracy

- *We will stop when the money runs out*

- Involves all stakeholders, decisionmakers, and technical experts
- Involves technical experts as principals
- Each participant plays a constructive role in clearly defining:
  - The problem
  - Data the decisionmaker needs to resolve that problem
  - Why the decisionmaker needs that type and quality of data
  - The tolerable decision error rates
  - How the decisionmaker will use the data to make a defensible decision
- Encourage efficient planning by framing and organizing complex issues
- Promotes communication among the stakeholders
- Documentation provides project management with a more efficient and consistent transfer of knowledge to new project members

- Brings together the stakeholders, decisionmakers, and technical experts at the beginning of the project to obtain commitment for the project and a consensus on the nature of the problem and the desired decision.

- Involves radioanalytical and other technical experts as principals to ensure the decisionmakers. data requirements and the results from the field and radioanalytical laboratory are linked effectively.

- Enables each participant to play a constructive role in clearly defining:

  - The problem that requires resolution;

  - What type, quantity, and quality of data the decisionmaker needs to resolve that problem;

  - Why the decisionmaker needs that type and quality of data;

  - What are the tolerable decision error rates; and

  - How the decisionmaker will use the data to make a defensible decision.

- Encourages efficient planning by framing and organizing complex issues.

- Promotes timely, open, and effective communication among the stakeholders, resulting in well-conceived and documented plans.

- Documentation provides project management with a more efficient and consistent transfer of knowledge to new project members.

1. State the problem

2. Identify the decision

3. Specify the decision rule and the tolerable decision error rates

4. Optimize the strategy for obtaining data

1. *State the problem*:
   - Describe clearly the problem(s) facing the stakeholder or customer.
2. *Identify the decision*:
   - Define the decision(s) or the alternative actions that will address the problem(s)
   - Define the inputs and boundaries to the decision.
3. *Specify the decision rule and the tolerable decision error rates*:
   - Develop a decision rule to get from the data to the desired decision
   - Define the limits on the decision error rates that will determine the type and amount of data needed.
4. *Optimize the strategy for obtaining data*:
   - Determine the optimum, cost-effective way to reach the decision while satisfying the desired quality of the decision.

Step 1   State the Problem.
Define the problem that necessitates the study,
identify the planning team, examine budget, schedule

} 1. State the problem

Step 2   Identify the Goal of the Study.
State how environmental data will be used in meeting objectives and
solving the problem. Identify study questions, define alternative outcomes

Step 3   Identify Information Inputs.
Identify data & information needed to answer study questions

Step 4   Define the Boundaries of the Study
Specify the target population & characteristics of interest,
define spatial & temporal limits, scale of inference

Step 5   Develop the Analytic Approach
Define the parameter of interest, specify the type of inference,
and develop the logic for drawing conclusions from findings

} 2. (a) (b) & (c)
Identify the decision

*Decision making
(hypothesis testing)*

*Estimation and other
analytic approaches*

Step 6.   Specify Performance or Acceptance Criteria

| Specify probability limits for false rejection and false acceptance decision errors | Develop performance criteria for new data being collected or acceptable criteria for existing data being considered for use |

} 3. (a) & (b)
Specify the decision rule and the
tolerable decision error rates

Step 7.   Develop the Plan for Obtaining Data
Select the resource-effective sampling and analysis plan
that meets the performance criteria

} 4. Optimize the strategy
for obtaining data

DQO Process Steps 1-4

Step 1. State the Problem.
Define the problem that necessitates the study;
identify the planning team, examine budget, schedule

Step 2. Identify the Goal of the Study.
State how environmental data will be used in meeting objectives and
solving the problem, identify study questions, define alternative outcomes

Step 3. Identify Information Inputs.
Identify data & information needed to answer study questions.

Step 4. Define the Boundaries of the Study
Specify the target population & characteristics of interest,
define spatial & temporal limits, scale of inference

DQO Process Steps 5-7

Step 5 Develop the Analytic Approach.
Define the parameter of interest, specify the type of inference,
and develop the logic for drawing conclusions from findings

Decision making | *Estimation and other*
(hypothesis testing) | *analytic approaches*

Step 6. Specify Performance or Acceptance Criteria

| Specify probability limits for false rejection and false acceptance decision errors | Develop performance criteria for new data being collected or acceptable criteria for existing data being considered for use |

Step 7. Develop the Plan for Obtaining Data

Select the resource-effective sampling and analysis plan
that meets the performance criteria

Should we take action to prevent exposure via milk from cows upwind or downwind?

Example Scenario

Does the milk from downwind cows have higher ^{90}Sr concentrations than that from upwind cows?

Downwind of Source

Potential Source of ^{90}Sr

Upwind of Source

2. Directed Planning Process   9

"Is there a problem?"

"too much" → how much ⊳ to measure

will take action it ⊳ too high

1. State the Problem
(Section 2.5.1)

Information Needed by the Project Planning Team	Radioanalytical Specialists Participation / Input	Output / Product
• Facts relevant to current situation (e.g., site history, ongoing studies). • Analytes of concern or analytes driving risk. • Matrix of concern. • Regulatory requirements and related issues. • Existing data and its reliability. • Known sampling constraints. • Resources and relevant deadlines.	• Evaluate existing radiological data for use in defining the issues (e.g., analytes of concern). • Assure that the perceived problem is really a concern by reviewing the underlying data that are the basis for the problem definition. • Consider how resource limitations and deadlines will impact measurement choices. • Use existing data to begin to define the analyte of concern and the potential range of concentrations.	• Problem defined with specificity. • Identification of the primary decision-maker, the available resources, and constraints.

From MARLAP Table 2.1

REASON FOR MAKING THE DECISION

2a. Identify the Decision(s)
(Section 2.5.2)

Information Needed by the Project Planning Team	Radioanalytical Specialists Participation / Input	Output / Product
• Analytical aspects related to the decision. • Possible alternative actions. • Sequence and priority for addressing the problem.	• Available protocols for sampling and analysis. • Provide focus on what analytes need to be measured, considering analyte relationships and background. • Begin to address the feasibility of different analytical protocols. • Begin to identify the items of the APSs. _Analytical Problem Spec_ • Begin to determine how sample collection and handling will affect MQOs.	• Statements that link the defined problem to the associated decisions and alternative actions.

↳ meas. qual. obj.

From MARLAP Table 2.1

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2b. Identify Inputs to the Decisions
(Section 2.5.2.2)

Information Needed by the Project Planning Team	Radioanalytical Specialists Participation / Input	Output / Product
• All useful existing data. • The general basis for establishing an action level. • Acquisition strategy options (if new data are needed).	• Review the quality and sufficiency of the existing radiological data. • Identify alternate analytes.	• Defined list of needed new data. • Define the characteristic or parameter of interest (analyte/matrix). • Define the action level. • Identify estimated concentration range for analytes of interest.

From MARLAP Table 2.1

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2c. Define the Decision Boundaries
(Section 2.5.2.3)

Information Needed by the Project Planning Team	Radioanalytical Specialists Participation / Input	Output / Product
• Sampling or measurement timeframe. • Sampling areas and boundaries. • Subpopulations. • Practical constraints on data collection (season, equipment, turnaround time, etc.). • Available protocols.	• Identify temporal trends and spatial heterogeneity using existing data. • With the sampling specialists, identify practical constraints that impact sampling and analysis. • Determine feasibility of obtaining new data with current methodology. • Identify limitations of available protocols.	• Temporal and spatial boundaries. • The scale of decision.

From MARLAP Table 2.1

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3a. Develop a Decision Rule
(Section 2.5.3)

Information Needed by the Project Planning Team	Radioanalytical Specialists Participation / Input	Output / Product
• Statistical parameter to describe the parameter of interest and to be compared to the action level. • The action level (quantitative). • The scale of decisionmaking.	• Available protocols for sampling and analysis. • Identify potentially useful methods. • Estimate measurement uncertainty and detection limits of available analytical protocols.	• A logical, sequential series of steps ("if...then") to resolve the problem.

From MARLAP Table 2.1

3b. Specify Limits on Decision Error Rates
(Section 2.5.3)

Information Needed by the Project Planning Team	Radioanalytical Specialists Participation / Input	Output / Product
• Potential consequences of making wrong decisions. • Possible range of the parameter of interest. • Allowable differences between the action level and the actual value. • Tolerable level of decision errors or confidence.	• Assess variability in existing data for decisions on hypothesis testing or statistical decision theory. • Evaluate whether the tolerable decision error rates can be met with available laboratory protocols, or if the error tolerance needs to be relaxed or new methods developed.	• Defined baseline condition (null hypothesis) and quantitative estimates of acceptable decision error rates. • Defined range of possible parameter values where the consequence of a Type II decision error is relatively minor (gray region).

From MARLAP Table 2.1

4. Optimize the Strategy for Obtaining Data
(Section 2.5.4)

Information Needed by the Project Planning Team	Radioanalytical Specialists Participation / Input	Output / Product
• All outputs from all previous elements including parameters (analytes and matrix) of concern, action levels, anticipated range of concentration, tolerable decision error rates, boundaries, resources, and practical constraints. • Available protocols for sampling and analysis. From MARLAP Table 2.1	• Sample preparation, compositing, subsampling. • Available protocols. • Methods required by regulations (if any). • Detection and quantitation capability. • Achievable MQOs by method, matrix, and analyte. • QC sample types, frequencies, and evaluation criteria. • Sample volume, field processing, preservatives, and container requirements. • Realistic MQOs for sample analysis. • Complete parameters for the APSs. • Resources and timeframe to develop and validate new methods, if required.	• Available protocols for sampling and analysis. • The most resource-effective sampling and analysis design that meets the established constraints (i.e., number of samples needed to satisfy the DQOs and the tolerable decision error rates). • A method for testing the hypothesis. • MQOs and the statement(s) of the APSs. • The process and criteria for data assessment.

MARLAP Recommends...
(Section 2.8)

- Using a **directed project planning process**
- **Radioanalytical specialists** be a part of the integrated effort of the project planning team
- The planning **process rationale be documented** and the documentation integrated with the project plan documents
- A **graded approach** in which the sophistication, level of QC and oversight, and resources applied are appropriate to the project

DQOs and the Development of MQOs

Module 3

Carl V. Gogolak

DQOs define the performance criteria that limit the probabilities of making decision errors by:

- Considering the purpose of collecting the data
- Defining the appropriate type of data needed
- Specifying tolerable probabilities of making decision errors

�&EPA

United States Office of Environmental EPA/100-06/001
Environmental Protection Information February 2006
Agency Washington, DC 20460

Guidance on Systematic Planning Using the Data Quality Objectives Process

EPA QA/G-4

U.S. Environmental Protection Agency (EPA). 2006. *Guidance for the Data Quality Objective Process* (EPA QA/G-4). EPA/240/B-06/001, Washington, DC. Available at www.epa.gov/quality1/qa_docs.html.

MARLAP Section 2.5 and Appendix B.

2

DQOs apply to both sampling and analysis activities

MQOs can be viewed as the analytical portion of the overall project DQOs

MQOs are the part of the project DQOs that apply to the measured activity result and its associated uncertainty

Multi-Agency Radiological
Laboratory Analytical Protocols Manual
Volume I. Chapters 1 – 9 and Appendices A - E

PLANNING

MARLAP

ASSESSMENT   IMPLEMENTATION

FDA   ≋USGS   NIST

July 2004
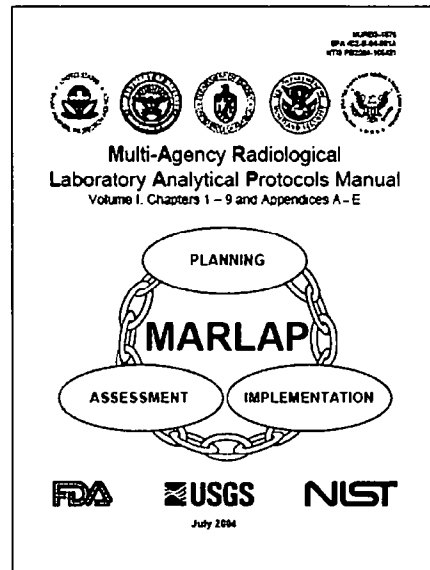
MARLAP Section 3.3.7

MQOs are statements of performance objectives or requirements for a particular analytical method performance characteristic. For example:
- Method uncertainty
- Detection capability
- Ruggedness
- Specificity
- Range

In a performance-based approach:
- MQOs are used initially for the selection and evaluation of analytical protocols
- MQOs are subsequently used for the ongoing and final evaluation of the analytical data

The most important MQO is the analytical uncertainty at a specified concentration (the action level)

MARLAP Section 3.3.7.1

Measurement Uncertainty

Uncertainty defined:

"A parameter associated with the result of a measurement that characterizes the dispersion of values that could reasonably be attributed to the measurand." [GUM]

The uncertainty of a measured value is typically expressed as an estimated standard deviation, called a *standard uncertainty*

Guide to the Expression of Uncertainty in Measurement

First edition 1995
ISBN 92-67-10188-9

© International Organization for Standardization 1993

Printed in Switzerland

NIST Technical Note 1297
1994 Edition

Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results

Barry N. Taylor and Chris E. Kuyatt

Physics Laboratory
National Institute of Standards and Technology
Gaithersburg, MD 20899-0001

(Supercedes NIST Technical Note 1297, January 1993)

September 1994

free download

3. DQOs and the Development of MQOs

5

- Refer to Attachment 3A in the course book behind Tab 13. Refer to NIST TN1297.
- International Organization for Standardization (ISO). 1995. *Guide to the Expression of Uncertainty in Measurement*. ISO, Geneva, Switzerland.
- The ISO *Guide to the Expression of Uncertainty in Measurement*, or GUM, 1995, is available in U.S. ($25) and international ($92) editions. The editions contain the same material, differing only in decimal marker, spelling, and size. The ISO *International Vocabulary of Basic and General Terms in Metrology* (VIM), 1993, a companion document to the GUM, is available only in an international edition ($71). The U.S. edition of the GUM is: *American National Standard for Expressing Uncertainty—U.S. Guide to the Expression of Uncertainty in Measurement*, ANSI/NCSL Z540-2-1997.
- NIST Technical Note 1297. Taylor, B.N. and C.E. Kuyatt (2003). *Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results*. National Institute of Standards and Technology (NIST), Gaithersburg, MD 20899-0001. Technical Note 1297. Available at: http://physics.nist.gov/Pubs/pdf.html (pdf) and http://physics.nist.gov/Pubs/guidelines/contents.html (html). Based on the comprehensive International Organization for Standardization (ISO) publication, *Guide to the Expression of Uncertainty in Measurement*.

American National Standards Institute
105-111 South State Street
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(fax) 212-302-1286

ISO Central Secretariat
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Case postale 56
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SWITZERLAND

No measurement program or sampling plan can be adequately designed without some estimate of the uncertainty in the data relative to the action level.

*If there were **no** measurement uncertainty and **no** spatial variability, how many measurements would be needed to find the average concentration of a radionuclide in an area?*
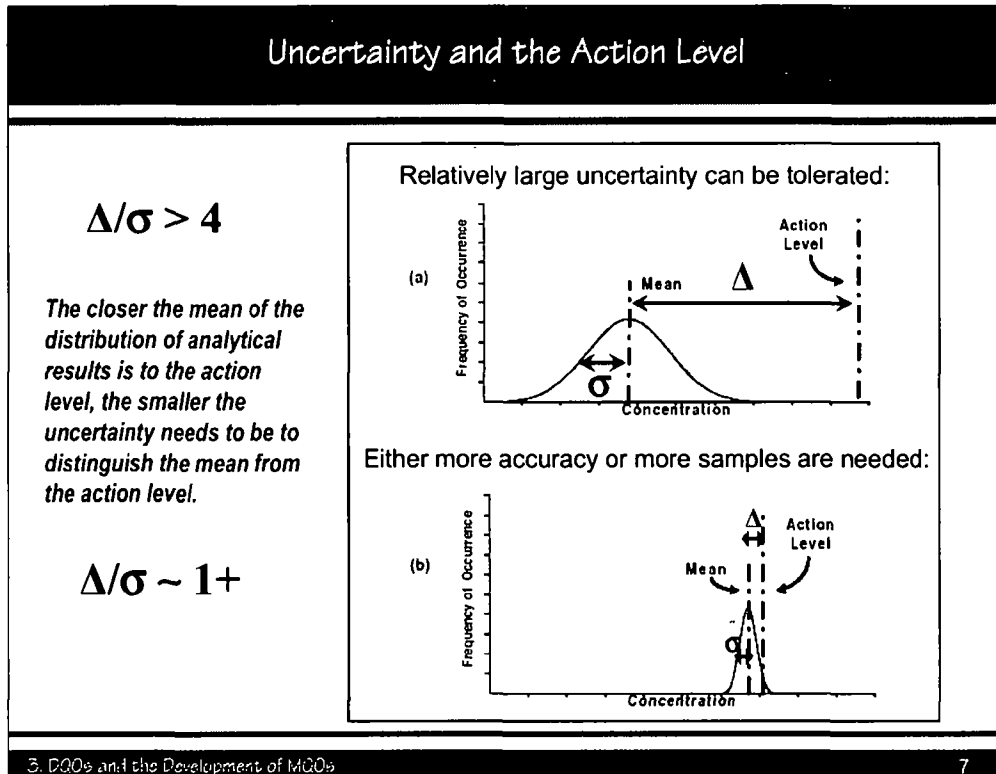
+ temporal

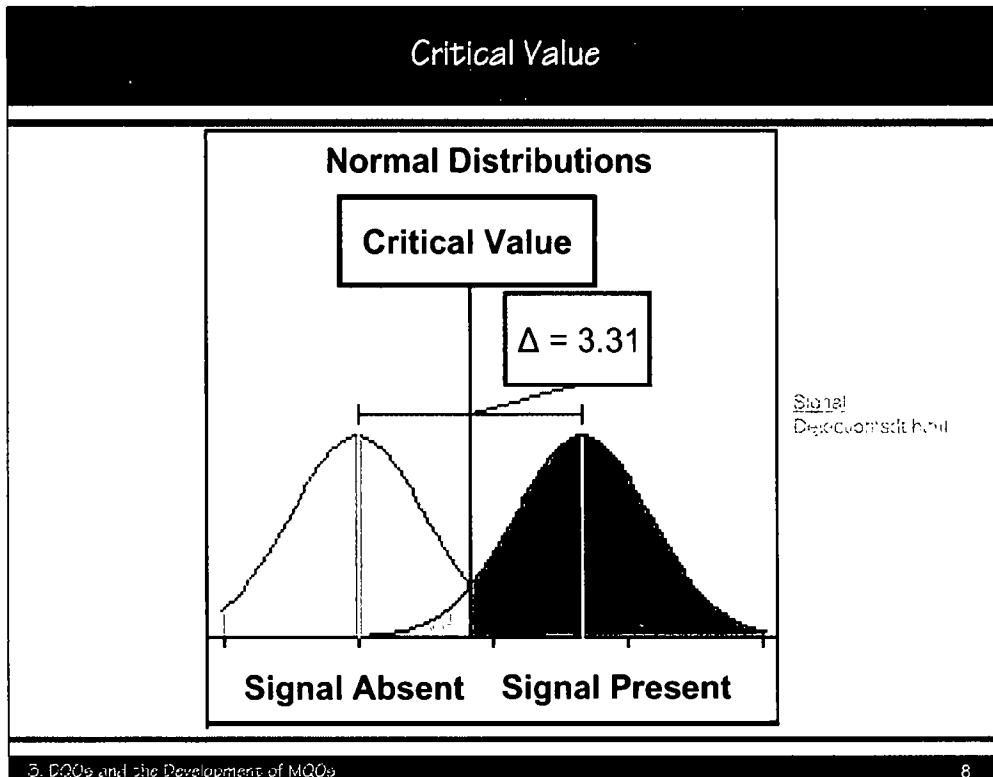Total uncertainty = measurement uncertainty + spatial variability

usually bigger

The answer to this question reveals why several samples are usually averaged. To reduce the decision maker's uncertainty by reducing both measurement uncertainty and spatial variability.

Planning is required to know how many samples are actually necessary to make good decisions.

Uncertainty and the Action Level

$\Delta/\sigma > 4$

The closer the mean of the distribution of analytical results is to the action level, the smaller the uncertainty needs to be to distinguish the mean from the action level.

$\Delta/\sigma \sim 1+$

Relatively large uncertainty can be tolerated:

Either more accuracy or more samples are needed:

3. DQOs and the Development of MQOs   7

- Figure B.10 appears in MARLAP Appendix B.3.8, page B-24.

- Δ/σ is the relative shift referred to in Appendix B, Section B.3.7. Gray region is referred to in Chapter 3. Δ is defined by the picture.

- At some concentration less than or equal to the action level, there is a *critical value* of the concentration. Critical level is sometimes abbreviated "L_C".

- Above this *critical level*, the decision maker will decide that the measured concentration is to high to continue to believe that the average concentration is truly less than the action level.

- *action level* (1.4.9): The term *action level* is used in this document to denote the value of a quantity that will cause the decisionmaker to choose one of the alternative actions. The *action level* may be a *derived concentration guideline level (DCGL)*, background level, release criteria, *regulatory decision limit*, etc. The *action level* is often associated with the type of media, *analyte* and concentration limit. Some *action levels*, such as the release criteria for license termination, are expressed in terms of dose or risk. See *total effective dose equivalent (TEDE)* and *committed effective dose equivalent (CEDE)*.

- *critical value (SC)* (3B.2): In the context of *analyte* detection, the minimum measured value (e.g., of the instrument signal or the *analyte* concentration) required to give confidence that a positive (nonzero) amount of *analyte* is present in the material analyzed. The critical value is sometimes called the *critical level* or *decision level*.

- *gray region* (1.6.3): The range of possible values in which the consequences of decision errors are relatively minor. Specifying a *gray region* is necessary because variability in the *target analyte* in a population and *imprecision* in the measurement system combine to produce variability in the data such that the decision may be .too close to call. when the true value is very near the *action level*. The *gray region* establishes the minimum distance from the *action level* where it is most important that the *project planning team* control *Type II errors*.

- *uncertainty* (1.4.7): The term .uncertainty. is used with several shades of meaning in MARLAP. In general it refers to a lack of complete knowledge about something of interest; however, in Chapter 19 it usually refers to .uncertainty (of measurement).

- *uncertainty (of measurement)* (3.3.4): .Parameter, associated with the result of a measurement, that characterizes the dispersion of the values that could reasonably be attributed to the *measurand*. (ISO, 1993a).

Critical Value

Normal Distributions

Critical Value

$\Delta = 3.31$

Signal
Detector's ...

Signal Absent   Signal Present

3. DQOs and the Development of MQOs   8

MARLAP Attachment B2, *Decision Error Rates and the Gray Region for Detection Decisions.*

A critical value (or critical level) is used in <u>hypothesis testing.</u> In this example It is the value that the test <u>statistic</u> must exceed in order for the null <u>hypothesis</u> to be rejected.

A **critical value** is a value determined in advance to decide whether a hypothesis will be accepted or rejected. If an observed value is **at or beyond** the critical value (in the **rejection region**), the hypothesis is **rejected**; otherwise (if the observed value is in the **acceptance region**), the hypothesis is accepted. Note that the critical value divides all possible values of the test statistic into these two regions, the rejection region and the acceptance region.

Connecting the MQOs to the DQOs

- Decision errors are possible because there is uncertainty in the data

- One part of the uncertainty is analytical measurement uncertainty

- Variation among samples with space or time also adds uncertainty

- To limit decision errors, the analytical measurement uncertainty should be limited to a level appropriate to the DQOs

How can you do that before you have any data?

MARLAP Appendix C, provided at Tab 13..

MARLAP Emphasizes Developing an MQO for Method Uncertainty

Developing a process to specify a required maximum method uncertainty

Method Uncertainty refers to the *predicted* uncertainty of a measured value that would be calculated if the method were applied to a hypothetical laboratory sample with a specified analyte concentration

Method uncertainty is a characteristic of the analytical method and the measurement process ALL SOURCES

Measurement uncertainty is a characteristic of an individual measurement

3. DQOs and the Development of MQOs

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See Section 3.3.7 and page 8 of chapter 1.

Data are collected so that decisions can be made about ...

- ... individual samples...*as for bioassays* /monitoring/

- ... the mean of a sampled population ... *as for MARSSIM final status surveys*

MARSSIM = *Multi-Agency Radiation Survey and Site Investigation Manual.*

MARSSIM provides guidance on how to design and implement a study to demonstrate that a site meets appropriate release criteria.

Website: http://www.epa.gov/radiation/marssim/

A decision rule has three parts:

- Parameter of Interest
- Action Level
- Alternative Actions ⟶ *should be input r*) *not* "part of"

Examples

- *If the activity of a sample exceeds a certain level, conclude the sample contains the radionuclide(s) of interest; otherwise conclude it does not.*

- *If the mean concentration in an area is less than the action level, conclude the area meets release criteria; otherwise conclude that corrective action must be taken.*

MARLAP Appendix B.

The decision rule will be applied by:

- Collecting data
- Computing test statistic related to the parameter of interest
- Conducting a statistical hypothesis test

Examples

- *If the counts from a sample exceed a certain level, conclude the sample truly contains the radionuclide(s) of interest; otherwise conclude it does not*

- *If the mean concentration from a set of samples is less than the action level, conclude the true concentration in the area from which the samples were taken meets release criteria; otherwise conclude that corrective action must be taken*

MARLAP Appendix B.3.6.

Decision Rules

The decision maker and planning team must be completely comfortable with the decision rule regarding the criteria for taking action

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MARLAP Appendix B.3.6.

Statistical Hypothesis Tests

- Statistical hypothesis-testing provides a mechanism for deciding between two mutually exclusive statements based on the value of a test statistic calculated from the data.

- These statements are called the null hypothesis, H_0, and the alternative hypothesis, H_1.

- The null hypothesis is assumed to be true unless the value of the test statistic obtained is very improbable under that assumption. In that case the data are deemed inconsistent with the null hypothesis. Therefore, it is rejected and the alternative hypothesis is chosen instead.

MARLAP Appendix B.3.7 and Appendix C.2.

DECISION	TRUE STATE	CONSEQUENCES
Reject H_0 …	… when it is actually true	Type I error (probability α)
Deciding not to reject H_0 …	… when it is actually false	Type II error (probability β)

MARLAP Appendix B, Table B-1.

(handwritten annotations):

EF H_0 = things are the same

Actually FALSE POSITIVE

Rβ FALSE NEGATIVE

Defining "Burden of Proof"

H_0: Sample contains no radioactivity

H_1: Sample contains radioactivity

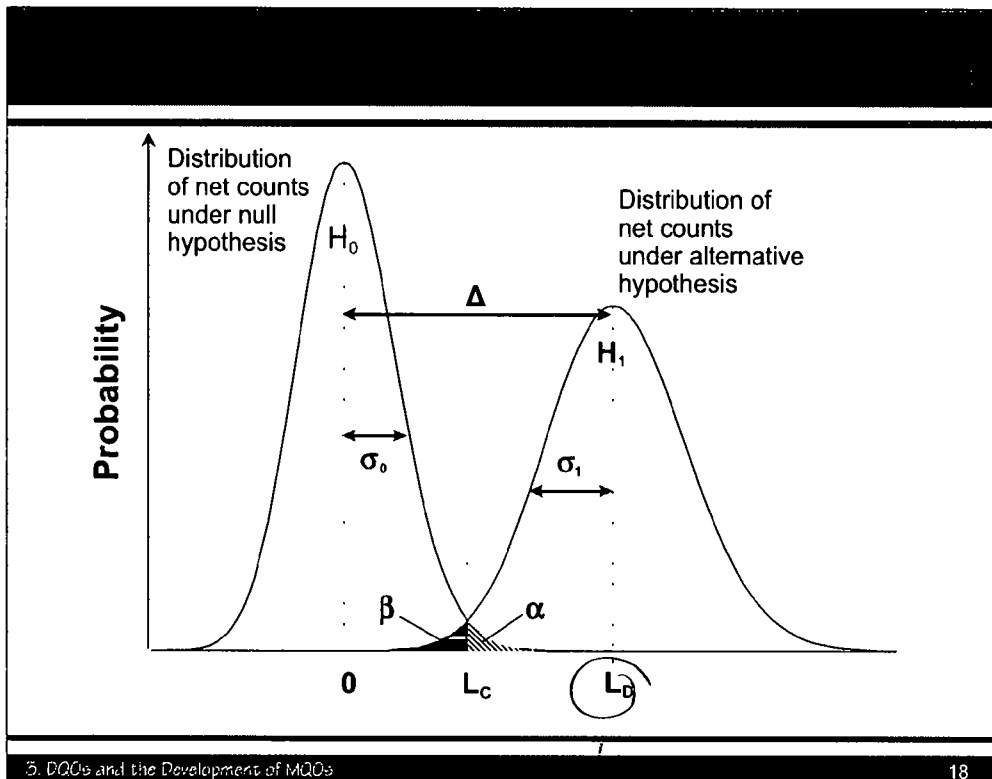Type I error: Decide there is radioactivity when there isn't   *FALSE POSITIVE*

Type II error: Decide there is no radioactivity when there is   *FALSE NEGATIVE*

This is the familiar framework for MDC calculations

Refer to MARLAP Attachment 3B, MARLAP Section B.3.7, and MARLAP Attachment B2 (Tab 13 of this course book).

• Decisions made on individual samples.
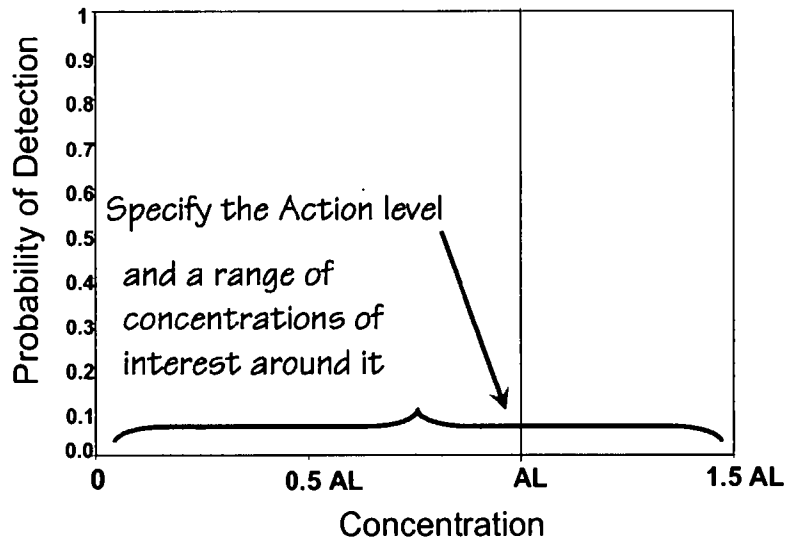
• The MDC problem.

Refer to MARLAP Attachment 3B and MARLAP Attachment B2 (Tab 13 of this course book).

- Decisions made on individual samples.
- The MDC problem.

Instrument reading

$= MDC$

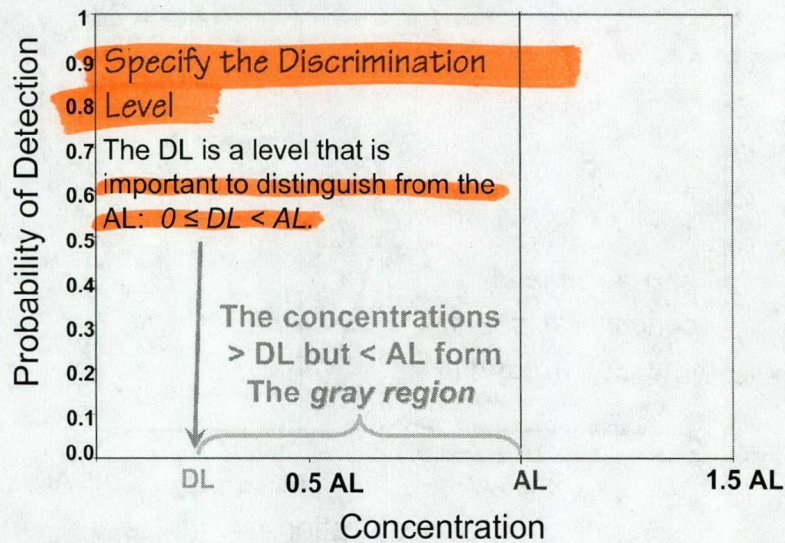Move to Δ β, α

$$\alpha = f(1 - \beta)$$

For example purposes, the range has been used as 0-1.5 times the action level.

Decisions made on individual samples. The MDC problem.

Refer to MARLAP Section B.3.7 and MARLAP Attachment B2 (Tab 13 of this course book).

• Decisions made on individual samples.

• The MDC problem.

Specify the Discrimination Level

The DL is a level that is important to distinguish from the AL: $0 \leq DL < AL$.

The concentrations > DL but < AL form The *gray region*

Probability of Detection

Concentration: DL, 0.5 AL, AL, 1.5 AL

3. DQOs and the Development of MQOs

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Refer to MARLAP Section B.3.7 and MARLAP Attachment B2 (Tab 13 of this course book).

- Decisions made on individual samples.
- The MDC problem.

Refer to MARLAP Section B.3.7 and MARLAP Attachment B2 (Tab 13 of this course book).

• Decisions made on individual samples.

• The MDC problem.

Specify Desired Limit on the Probability of Type I Decision Errors

Gray Region

Limit the probability of flagging a blank sample by specifying α at the DL

Probability of Detection
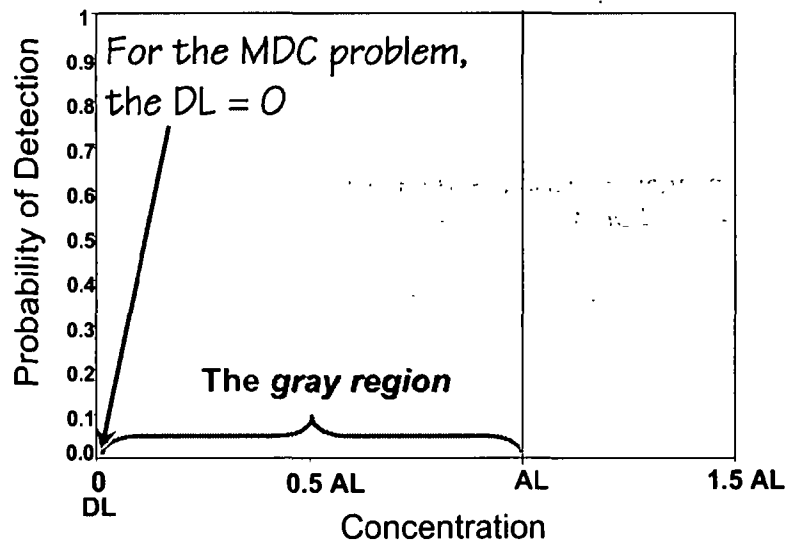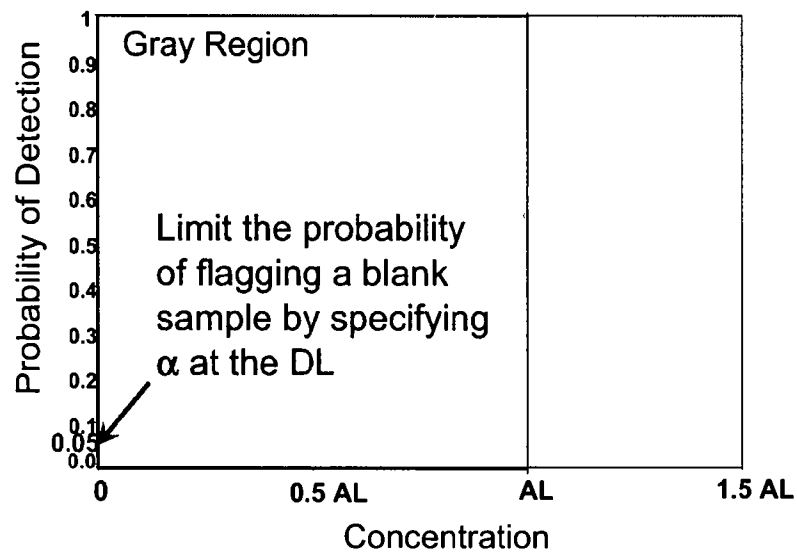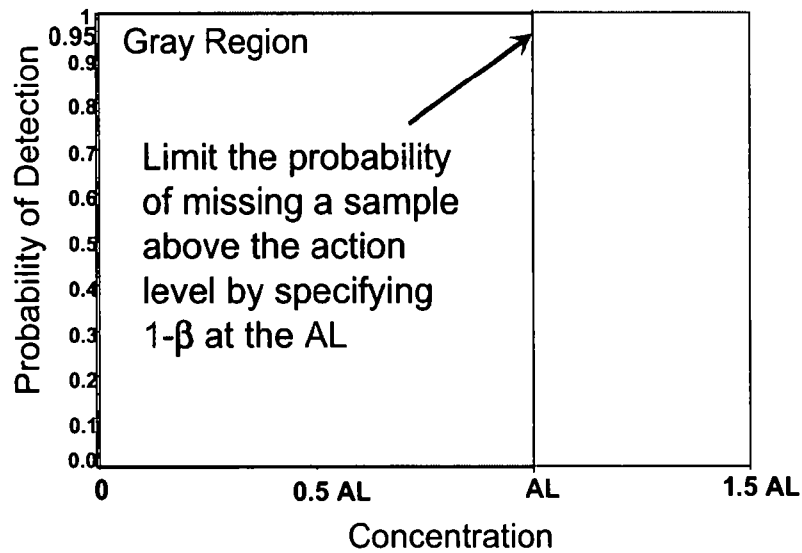
Concentration

0   0.5 AL   AL   1.5 AL

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Refer to MARLAP Section B.3.7 and MARLAP Attachment B2 (Tab 13 of this course book).

• Decisions made on individual samples.

• The MDC problem.

Specify Desired Limit on the Probability of Type II Decision Errors

Gray Region

Limit the probability of missing a sample above the action level by specifying 1-β at the AL

Probability of Detection

Concentration

0.5 AL   AL   1.5 AL

Refer to MARLAP Section B.3.7 and MARLAP Attachment B2 (Tab 13 of this course book).

• Decisions made on individual samples.

• The MDC problem.

Refer to MARLAP Section B.3.7 and MARLAP Attachment B2 (Tab 13 of this course book).

• Decisions made on individual samples.

• The MDC problem.

Probability of Detection Increases with Concentration

True mean Concentration	Probability Measure > L_c
0.0	5%
1.0	26%
3.0	91%

True Concentration (in units of measurement standard deviation)
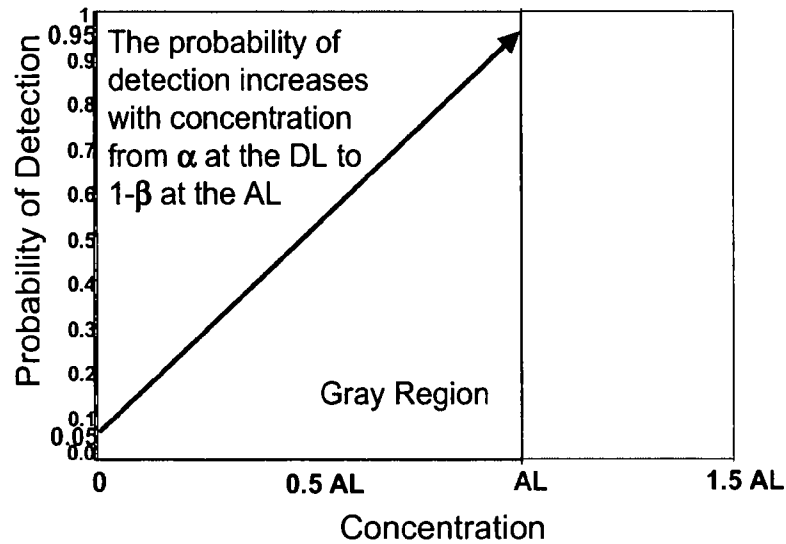
Refer to MARLAP Section B.3.7 and MARLAP Attachment B2 (Tab 13 of this course book).

• Decisions made on individual samples.

• The MDC problem.

Power Curve

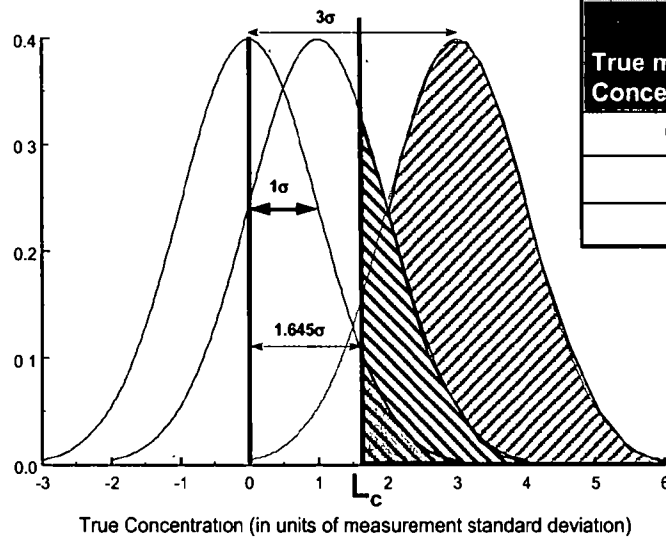| True mean Concentration	Probability Measure > L_c
3.0	91%
1.0	26%
0.0	5%

Refer to MARLAP Section B.3.7 and MARLAP Attachment B2 (Tab 13 of this course book).

- Decisions made on individual samples.
- The MDC problem.
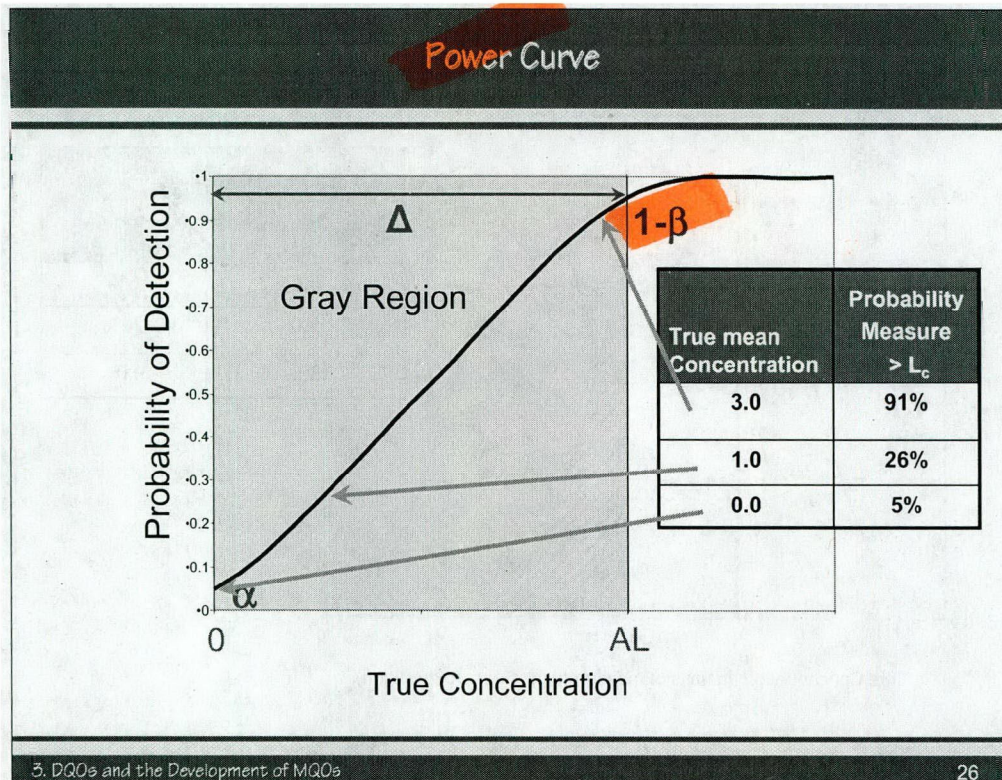- We can map the probabilities of exceeding the critical level as a function of true concentration from the previous slide onto a *power curve*.
- Here, the action level is 4 and $\sigma = 1$.

Receiver Operating Characteristic Curve (ROC)

Healy, M. R., Berger, D. E., Romero, *V. L., Aberson, C. L., & Saw, A.* 2002. *Signal Detection Theory Applet and Tutorial. Available online at http://wise.cgu.edu/sdt/*

Refer to MARLAP Section B.3.7 and MARLAP Attachment B2 (Tab 13 of this course book).

Calculating the Required Method Uncertainty

To limit the probability of decision errors, α and β, to 0.05,...

H_0

$\Delta = AL$

σ_0

H_1

σ_1

β

α

0   L_C L_D

...the standard deviation of the analytical method must be small enough that $\Delta/\sigma_1 > 1.645 + 1.645$.

$$\therefore \sigma_1 < AL/3.29$$
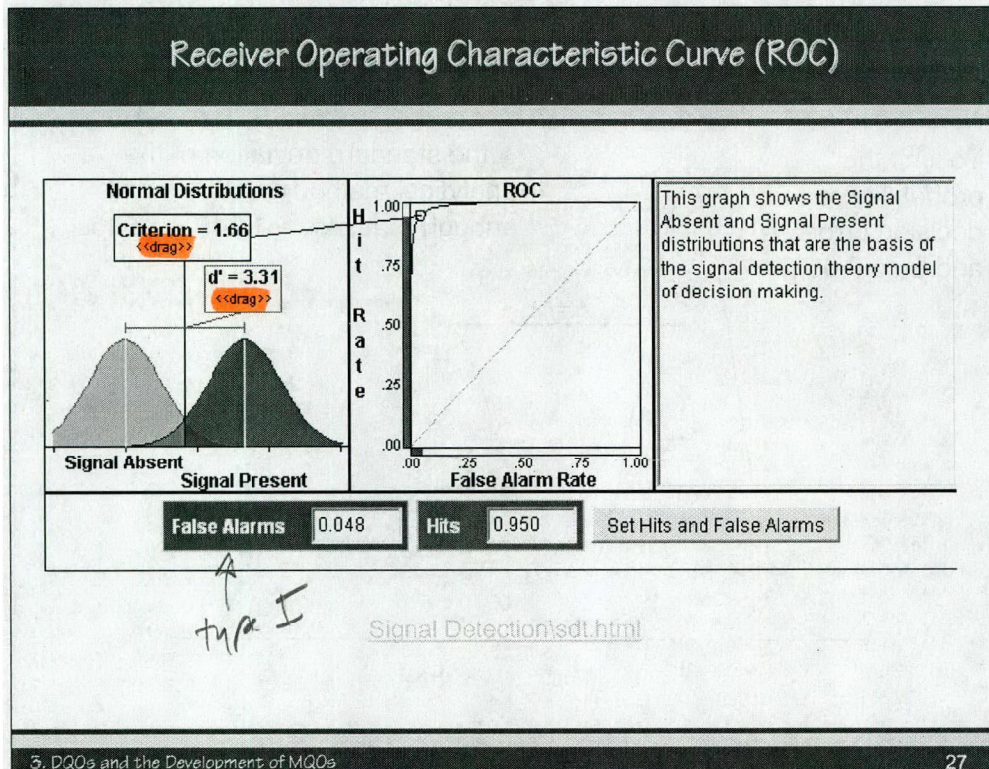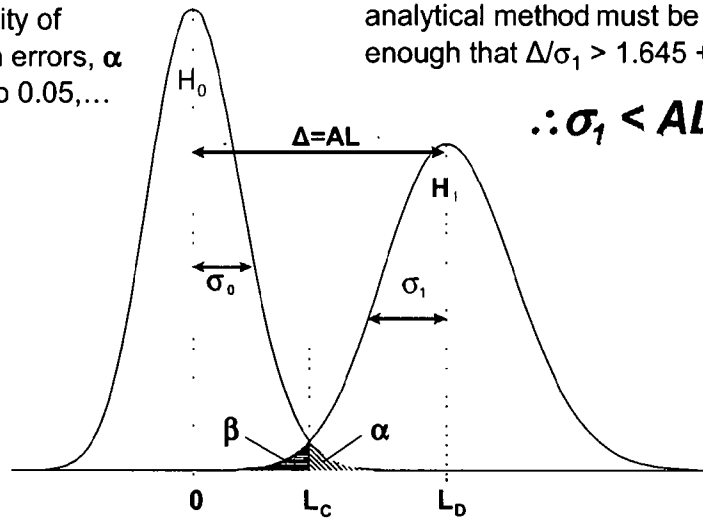
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Refer to MARLAP Appendix C.3, Scenario II and MARLAP Attachment B2 (Tab 13 of this course book).

• Decisions made on individual samples.

• The MDC problem.

The MQO for Method Uncertainty is the Required Method Uncertainty

The performance requirement is that the *upper bound* for the measurement standard deviation at the action level is

$$u_{MR} = \Delta / 3.29 \approx 0.3 \times AL$$

u_{MR} is the *required method uncertainty*

This is essentially the same as requiring that the MDC not exceed the action level because:

a) The minimum detectable concentration (MDC) is often found to be about 3 or 4 times the measurement uncertainty

b) MDC $\approx 3\ \sigma_{MR}$ implies $\sigma_{MR} \approx MDC / 3$

c) If MDC $< \approx AL$, then $\sigma_{MR} \approx AL/ 3 \approx 0.3 \times AL$

Refer to MARLAP Appendix C.3, Scenario II and MARLAP Attachment B2 (Tab 13 of this course book).

- Decisions made on individual samples.
- The MDC problem.

Example
    If the action level was 1 pCi/L, then the required method
    uncertainty would be
    $$u_{MR} = 0.3 \; AL = 0.3 \; pCi/L$$

    The laboratory's <u>estimate</u> of its measurement uncertainty
    at the action level is called *the method uncertainty*. This
    must not exceed the required method uncertainty.

Refer to MARLAP Appendix C.3, Scenario II and MARLAP Attachment B2 (Tab 13
of this course book).

• Decisions made on individual samples.

• The MDC problem.

Data are collected so that decisions can be made about ...

- ... individual samples...*as for bioassays*
- ... the mean of a sampled population ... *as for MARSSIM final status surveys*

Refer to MARLAP Appendix C.3 Scenario I and MARLAP Attachment B1.
The following series of slides consider the mean of a sampled population.

Decisions Made About the Mean of a Sampled Population

Decision Rule: If the true mean concentration in the survey unit is less than the action level it may be released for unrestricted use. Otherwise further remediation may be required.

H_0: The true mean exceeds the action level

H_1: The true mean is below the action level

- **Type I error**: Decide the true mean does not exceed AL when it does
- **Type II error**: Decide the true mean exceeds AL when it doesn't

- Sampled Population.
- Refer to MARLAP Appendix C.3 Scenario I and MARLAP Attachment B1.

Specify Gray Region and Desired Limits on the Probability of Decision Errors for True Concentrations at its Upper and Lower Boundaries
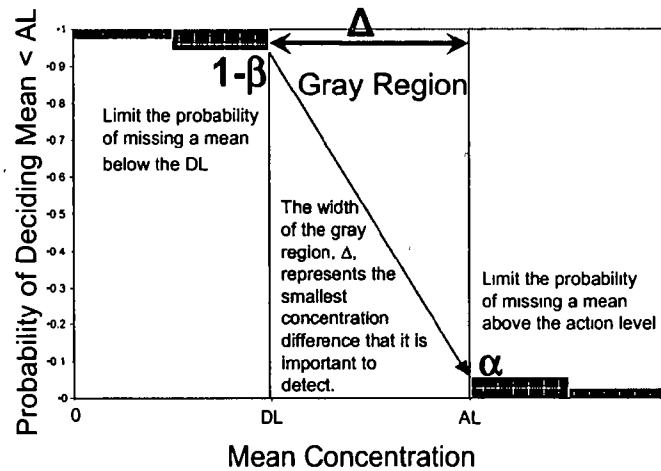
- Sampled Population.
- Refer to MARLAP Appendix C.3 Scenario I and MARLAP Attachment B1.

Probability of Deciding Mean < AL

1-β

Gray Region
Δ

α

0   DL   AL

Mean Concentration

Signal Detection power_applet.htm

3. DQOs and the Development of MQOs   34
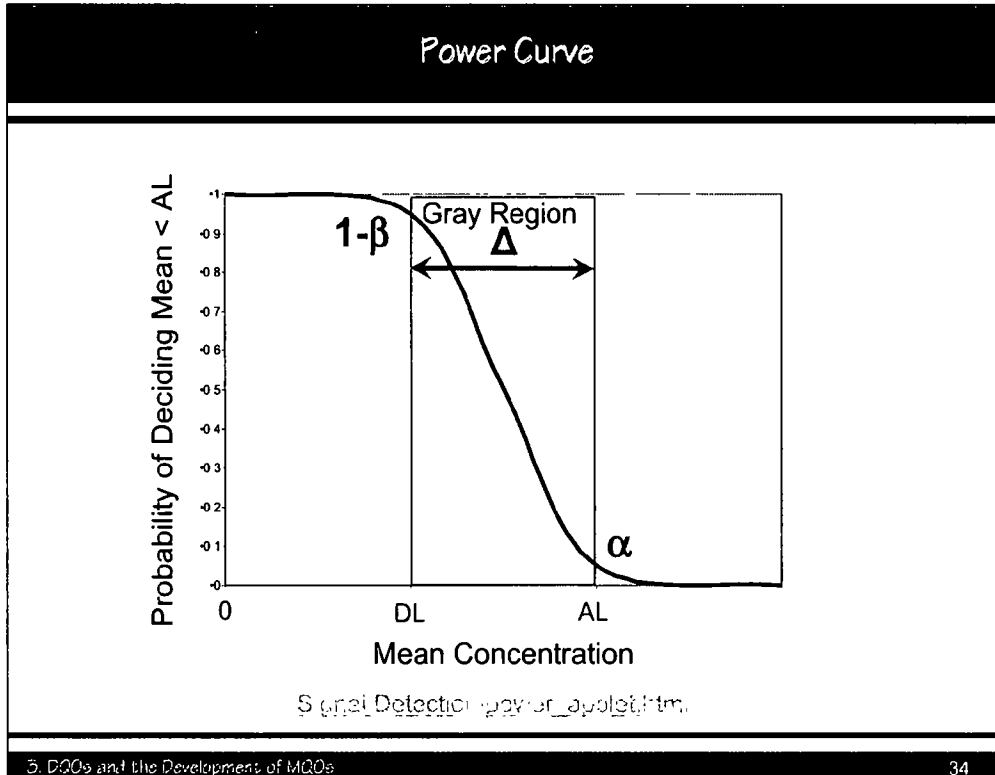
• Sampled Population.

• Refer to MARLAP Appendix C.3 Scenario I and MARLAP Attachment B1.

Healy, M. R., Berger, D. E., Romero, *V. L., Aberson, C. L., & Saw, A.* 2002. Claremont Colleges' "Web Interface for Statistics Education" (WISE) Power Applet. Available online at http://wise.cgu.edu/power/powerapplet1.html.

- The width of the gray region is $\Delta = AL - DL$

- The number of samples needed to conduct the hypothesis test with specified limits on α and β depends on the relative shift, Δ/σ

- To keep the number of samples reasonable, σ should be such that $1 < \Delta/\sigma < 3$. Ideally, $\Delta/\sigma \sim 3$

- The cost in samples required rises rapidly when $\Delta/\sigma < 1$, but there is little benefit from increasing Δ/σ above 3

- Sampled Population.
- Refer to MARLAP Appendix C.3 Scenario I and MARLAP Attachment B1.

Method Uncertainty as a Component of the Total Uncertainty

- The total variance of the data is $\sigma^2 = \sigma^2_M + \sigma^2_s$

- The sampling standard deviation, σ_S, depends on the variability in the spatial distribution of the analyte concentrations and other factors having to do with how the sampling is performed

- The analytical standard deviation, σ_M, is affected by laboratory sample preparation, subsampling and analysis procedures

- Sampled Population.
- Refer to MARLAP Appendix C.3 Scenario I and MARLAP Attachment B1.

Comparing final Single meas to Action Levels

The MQO for Method Uncertainty

Generally it is easier to control σ_M than σ_S

If σ_S is large, then the best one can do is make σ_M small relative to σ_S

How small is small enough?

If $\sigma_M \sim \sigma_S/3$, then the analytical method variance is contributing less than 10% to the total variance σ^2. Reducing it further will not reduce σ very much.

This implies that the upper bound for σ_M should be

$$u_{MR} = \frac{\sigma}{\sqrt{10}} = \frac{\Delta/3}{\sqrt{10}} = \frac{\Delta}{3\sqrt{10}} \approx \frac{\Delta}{10}$$

- Sampled Population.
- Refer to MARLAP Appendix C.3 Scenario I and MARLAP Attachment B1.

- If LBGR = 0, then u_{MR} = AL/10

- This is the same as requiring that the required *relative* standard deviation of the measurements, φ_{MR}, near the action level be 10%

- In other words, the minimum quantifiable concentration (MQC) should be no larger than the action level

  $\searrow$ relative $u_{MR} \geq 10\%$

This is for a sampled population.

The *minimum quantifiable concentration* (MARLAP Section 20.2.7) is the analyte concentration that gives measured results with a specified relative standard deviation 1 / k_Q, where k_Q is usually chosen to be 10.

The principal MQOs in any project will be defined by:

- The *required method uncertainty*, u_{MR}, below the *action level*

  AND

- The *relative method uncertainty*, φ_{MR}, above the *action level*

$$\varphi_{MR} = u_{MR} / AL$$

When making decisions about *individual samples* . . . . $u_{MR} \sim \Delta/3$

When making decisions about the *mean of several samples* . . $u_{MR} \sim \Delta/10$

Where Δ is the width of the gray region . . . . $\Delta = AL - DL$

Method Uncertainty: MARLAP's Common Thread

Definition:
- Predicted uncertainty of a measured value that would likely result from the analysis of a sample at a specified analyte concentration.
- Combines *imprecision* and *bias* into a single parameter whose interpretation does not depend on context.

MARLAP recommends:
- Identify the method uncertainty at a specified concentration (typically the *action level*) as an important method performance characteristic.
- Establish a measurement quality objective for method uncertainty for each analyte/matrix combination.

MQO for the method uncertainty (at a specified concentration):
- Links the three phases of the data life cycle: planning, implementation, and assessment.
- 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 <u>action level</u>, and the lower bound is termed the "<u>discrimination limit</u>."

Examples of MQOs for method uncertainty at a specified concentration:
- A method uncertainty of 0.01 Bq/g or less is required at the action level of 0.1 Bq/g.
- The method must be able to quantify the amount of ^{226}Ra present, given elevated levels of ^{235}U in the samples.

Terminology:
- u_{MR} Required method uncertainty (absolute)
- $\varphi_{MR} = u_{MR} / AL$ Required method uncertainty (relative)
- $\Delta = AL - DL$ Width of the gray region (range of values where the consequences of a decision error are relatively minor)
- Action level   Concentration that will cause a decisionmaker to choose one of the alternative actions
- Discrimination limit   Synonymous with the lower bound of the gray region

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Example Scenario

Does the milk from downwind cows have higher ^{90}Sr concentrations than that from upwind cows?

Downwind of Source

Potential Source of ^{90}Sr

Upwind of Source

3. DQOs and the Development of MQOs   40

- Action Level – 8 pCi/L limit for total ^{90}Sr in milk
- Average background level of 2-3 pCi/L for ^{90}Sr in milk
- Choose Discrimination Level at 3 pCi/g
- $\Delta = (AL\text{-}DL) = 8 - 3 = 5$

$$u_{MR} = \frac{\sigma}{\sqrt{10}} = \frac{\Delta}{3\sqrt{10}} \approx \frac{\Delta}{10}$$

$$u_{MR} = 5/10 = 0.5 \, pCi/L \quad \varphi_{MR} = 0.5/8 = 6\%$$

Power Curve

Required Method Uncertainty

$\varphi_{MR} = \pm 6\%$

Measured (y)

Above the action level, the bound on the *relative* standard deviation is constant and equal to

$\varphi_{MR} = u_{MR} / \text{AL}$

The required method uncertainty, u_{MR}, is specified at the action level

$u_{MR} = \pm 0.5 \text{ pCi/L}$

Below the action level, the bound on the standard deviation is constant and equal to u_{MR}

0   3   8
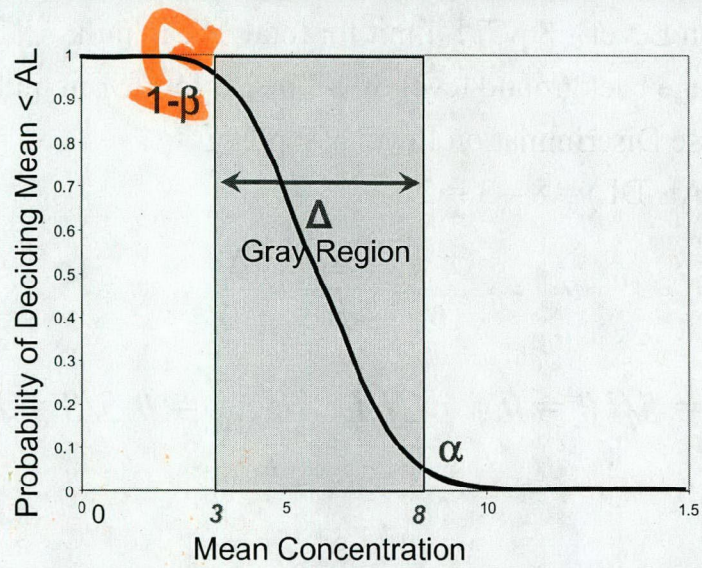
True Concentration (pCi/L)
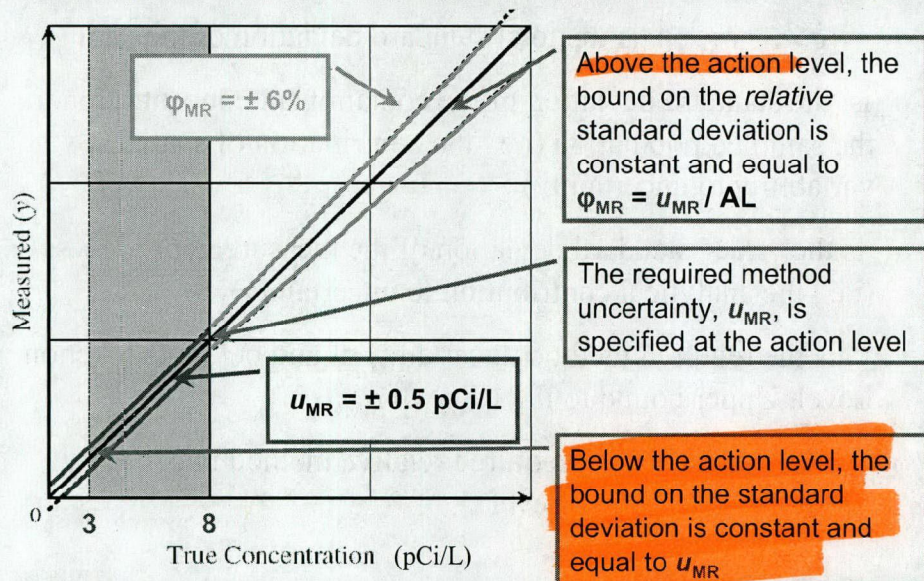
3. DQOs and the Development of MQOs

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Refer to MARLAP Appendix C.4.1 (Tab 13).

$\sigma = [\sigma_S^2 + \sigma_M^2]^{\frac{1}{2}}$ is the total standard deviation of the data

σ_S is the standard deviation of the contaminant concentration in the sampled population (i.e., the contribution of spatial variability to uncertainty)

σ_M is the "true" standard deviation of the measurement process (i.e., the analytical contribution to uncertainty)

u_{MR} is the required method uncertainty at and below the Action Level. Upper bound to the value of σ_M

$\varphi_{MR} = [u_{MR} / AL]$ is the required relative method uncertainty above the Action Level

Continued...

If the spatial variability is large, then $u_{MR} = \Delta/10$ would be the goal when measuring for the mean of a sampled population.

$u_{MR} = \Delta/3$ would be the goal when deciding whether an individual sample exceeds an AL.

If DL=0, these reduce to $u_{MR} = AL/10$ and $u_{MR} = AL/3$, respectively.

Δ is the width of the gray region

Δ = (Action Level – Discrimination Level) = (AL-DL) = (UBGR-LBGR)

α is the probability of a Type I decision error

β is the probability of a Type II decision error

α and β are often taken to be 0.05.

The required method uncertainty, u_{MR}, and the required method relative uncertainty, φ_{MR}, can be used for both method selection and to develop acceptance criteria for QC sample results.

Refer to MARLAP Appendix C.4.2.

Key Analytical Planning Issues: MQOs and APSs

Module 4

Bob Litman
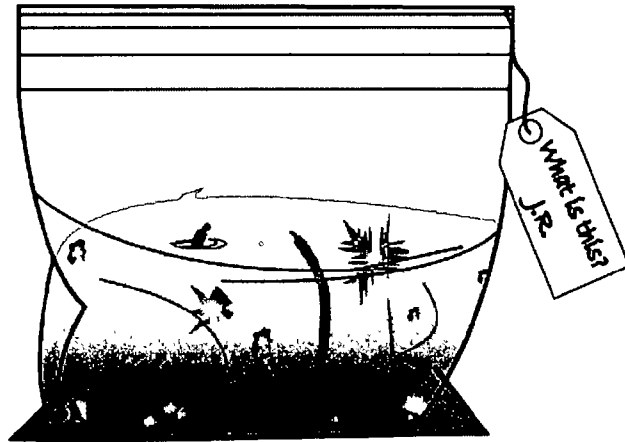
A zip-lock bag with mud, stones, and wire was left on my desk at a nuclear plant. The attached note from "J.R." was all the information received.

A system engineer had pulled this out of one of the feedwater heaters (it was labeled potentially contaminated but the heater was outside the radiologically controlled area).

He wanted to know, "What is the material made of and where did it come from?"

After a visual exam I told him rust from inside the condenser and the pre-heaters forward of this one.

"What about the chunks?" he asked.

I took out a microscope and prepared a slide. "It appears to be weld wire and weld slag", I said after the visual with the microscope.

"What about scaffolding material?" he asked.

I told him, "I'll need a couple of days to analyze for aluminum. How much scaffolding are we looking for?"

"A lot," he replied.

When I brought the sample to the lab (inside the RCA) I first did a gamma spectrometry analysis to see if the sample was contaminated. Sure enough it contained ^{60}Co and ^{58}Co. When I told this to the engineer he said, "Oh, that's interesting. But that's not important to what I need to know".

The engineer's PROJECT was to find out what the materials was made of to determine if it came from staging. What SPECIFICATION should he have made about the sample so that the ANALYTICAL process would have proceeded more smoothly?

Overview of the Analytical Process

The Project Manager must ensure that technically knowledgeable personnel write the Analytical Protocol Specification (APS), before sampling occurs.

When the APS is completed...

Project Manager is responsible for identifying processes that comprise the entire sample life:

- Sampling...
- ...through analysis...
- ...to data trending...
- ...and everything in between

The Project Manager needs to ask the right questions and ensure that the questions that relate to the sample processing are answered correctly.

All of this seems very obvious, but in reality it is seldom done!

A *key analytical planning issue* has a significant effect on the selection and development of analytical protocols or has the potential to be a significant contributor of uncertainty to the analytical process and, ultimately, the resulting data.

Minions
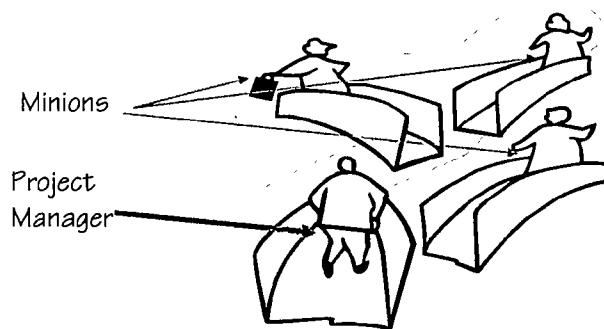
Project Manager

Project Manager is responsible for having the "vision" and entrusting his team specialists to find ways to implement the mission.

Need to know what we see as the end result so that the steps, from sampling to final data analysis, can support the end result.

What we are going to do is discuss the key planning issues discussed in Chapter 3.

Output of a directed planning process that contains the project's analytical data needs and requirements in an organized, concise form

The APSs represent the resolution and documentation of key analytical planning issues, many of which will be covered in this session.

The APS Will Contain....

The Analytical Protocol Specifications (APS) is the central planning document that contains important information:

- Specifics about the range of concentrations to be determined
- Potential interferences (radiological and non-radiological) that may eliminate several potential methods
- Amount of sample required, preservation, pretreatment, etc.
- The required method uncertainty, u_{MR}
- Many other factors effecting the analytical results

This information is used to construct the MQOs that will appear in the APS

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The APS must be completed *before* samples are collected or analyzed

- "If a ship captain does not know to which port he is steering, no wind is favorable"
- The next segment of the presentation deals with the specific items which need to be considered, detailed or eliminated when writing an APS.

"If you don't know where you're going, you'll probably end up somewhere else"

7

General

- Development of an analyte list   *wbt/dry basis*
- Concentration ranges   *units*
- Chain of custody

Matrix Specific

- Filtration of liquid samples
- Solid samples sieved to a particular mesh range
- …

Which radionuclides are we looking for?

Based on:

- Process knowledge
- Historical site assessment (HSA)
- Previous studies of this or similar sites
- Preliminary project studies

There are 2,540 radionuclides and 480 isomeric states of nuclides. The selection of what could possibly be in the site that is being assessed would be based on the radionuclide's half-life, how long before the site assessment the production or use of the radionuclide was present, and how much was there at anyone time.

What is the expected concentration range for each radionuclide in the samples we will be analyzing?

Based on:

- Historical site assessment (HSA)
- Existing data on expected "background" values

What might be one reason to anticipate why we need to know how much is present?

- Safety to samplers
- Safety to analysts
- Field *versus* laboratory analysis
- Potential laboratory methods
- Costs
- Sample size

What are the matrices in which the radionuclides can potentially be contained?

What needs to be evaluated about each matrix?

- Homogeneity/heterogeneity (commonly ignored)
- Potential hazards to sampler or analyst
- Chemical composition of the matrix
- Pretreatments prior to analysis

- What are examples of matrices: surface water, groundwater, soil, concrete, asphalt, gypsum, linoleum, etc.
- Will or should the samples be homogenized? In the field or by the lab?
- What are the contaminants in this matrix, besides what you're looking for, that may prove hazardous? For example, PCBs, explosives (H_2 in tank water), VOCs, asbestos, carbon monoxide, etc.
- "Solid" is not a matrix! Humic, sand, loam are different descriptors for soil. Linoleum? What is it made out of? Lab needs to know so that they can analyze it successfully.
- Does the groundwater sample need to be filtered, does the sandy soil sample need to be sieved, must the whole sample be used, must the whole sample be dissolved, ...?

- Parent-progeny
- Easy-to-detect as markers for hard-to-detect
- Process knowledge

- If medical waste is present and Tc-99m generators are part of the waste, what might be present that most likely will be undetected by gross alpha-beta analysis? Tc-99: parent daughter relationship plus process knowledge.
- Site produced ^{205}Pb by neutron bombardment of ^{204}Pb. What else might you expect? ^{204}Tl (half life 3.8 years) from (n,p) reactions.

All projects have schedules. Some considerations are:

- Existing method?

- Turn-around-time?

- Available funds?

These considerations may change --

Project phase... Screen

Analytical

Confirmation

etc.

- Does a validated method exist for the analyte matrix or does one need to be developed, and can it be done within the scope of work?

- Can an offsite laboratory get the results to the decision makers in a timely manner, or will an on-site lab need to be established"

- Will the funds available support the deadline based on the types of samples and analyses?

- In initial phases of the project, the time frame to get results may be shorter and require less precise measurement. As the analyte and matrix list is revised, the time to obtaining results may change and measurements may become more precise.

- Based on updated project information
- Should be a routine part of the project development to review these lists to ascertain if something (either an analyte or matrix) is:
  - Omitted
  - Unnecessary

Initially, you may know there is radioactive contamination. This could be one of 3,020 possible radioactive substances (this is a small list compared to the 2+ million known organic compounds!). As more information about the site becomes available, this list is pared down and the number of potential radionuclides and possible matrices decreases. This should be done at routine intervals in the early stages of the project and less frequently as time progresses.

Method Performance Characteristics and MQOs (3.3.7)

- Examples of Method Performance Characteristics
  - Method uncertainty
  - Method detection capability *Spec eqns*
  - Method range
  - Method specificity *unaffected by a Juke e.g. TDS in H₂O*
  - Method ruggedness *— unaffected by a Juke e.g. TDS in H₂O*
- An MQO is a quantitative or qualitative statement of a performance objective or requirement for a particular method performance characteristic
- MARLAP recommends that an MQO for method uncertainty (u_{MR}) be established for each radionuclide/matrix combination

This is where the Project Manager must hone the details of the project goals. The above information is critical to developing project MQOs based on the methods selected.

- Example MQO for minimum detectable concentration (MDC)
  - An MDC for ^{60}Co in water samples of 0.5 pCi/L for each sample
- Example MQO for required method uncertainty
  - A method uncertainty for ^{137}Cs in soil of 2 pCi/g at the action level of 20 pCi/g

Refer to the APS in the handout (Tab 14). What do we know about the historical data for the analysis of ^{90}Sr in milk?

What methods of analysis will we be using?

- Determined during the project planning phase
- Limiting analytical options based on
  - Historical
  - Known interferences
  - Known method limitations
- May be determined by presence of other radionuclides

Significant quantities of ^{232}Th can be determined directly by gamma spectrometry using the ^{228}Ac 911 keV gamma ray as long as there is confidence that the actinium is always supported in the matrices to be analyzed. However, the presence of ^{60}Co would cause significant background (from Compton) problems in that region of the gamma spectrum. This limits the analytical options to methods other than gamma spec if the MQOs cannot be achieved due to the presence of ^{60}Co.

- Does the method exist?
  - May require research and development
- Is the method validated for the project's matrices?
- Is it performed routinely enough to support the project activities?

Method validation is a concept that deals with the laboratory's experience with the method for the particular analyte in the particular matrix of your project. (More about method validation in Module 9 about Chapter 6.)

- Laboratory blank
- Matrix spike
- Laboratory control sample (LCS)
- Duplicate sample
- Matrix spike duplicate

Any or all of these may be chosen for the project. The radiochemical specialist. in coordination with the project team, needs to decide which ones should be used.

The first four will be discussed in more detail in Module 10 (on MARLAP Chapter 7), where we will discuss acceptance criteria for each of these. A Performance Evaluation/Testing sample (external program) is not considered a "lab QC Sample," but is an important part of the laboratory QA program and should be part of a laboratory's analytical load.

- Security
- Documentation

Samples are obtained and sometimes stored prior to shipment. Locked up? Refrigerated?

Who handled the sample? Must each person verify sample in their custody? What abcut shipping? Are all containers sealed with tamper proof tape? Original chain of custody returned to site? What about chain of custody at the laboratory?

- What format should data report have?   *Precision!!*
  - Results ±1, 2, or 3 (combined standard uncertainty)?
  - Units?
  - MDC, Critical Level, MQC, ...?   ← *Validation?*
- Two ID numbers—both should be on data report.   *Lab + Field*
- Particulars for each sample?
- Enough data to reproduce calculations?

There is no standard report format. The Project Manager must let the lab know the project data requirements.

What are the two ID numbers? The Project ID and the LAB ID.

- Sample container to be used?
- Whole sample to be analyzed, or how can representative sub-sampling be assured?
- Sample to be homogenized by laboratory?
- Spurious detritus in sample to be discounted/ discarded/analyzed separately?

How could sample container affect results? Filter papers stored in plastic containers-static charge could dislodge particulates...

Issue of subsampling in the laboratory is usually not addressed adequately. See MARLAP Appendix F (Volume II) for guidance.

What should the laboratory do with twig parts or plant roots in soil samples?

- Handout provides an APS for detection of ^{90}Sr in milk

- We will discuss each area of the APS and the significance of each specification

Refer to APS example behind Tab 14.

- Assume that the selection of the analyte list is completed based on historical assessment of the project
- Section 3.2 directs us to identify the matrices, concentration range and any chemical or radiological interferences

Describe the potential interferences (can be radioactive or non-radioactive):

- Calcium, milk fats, ^{40}K, fission products, magnesium

The anticipated concentration ranges to be needed:

- Is it expected that zero pCi/L will be found in Milk? What is the historical background for ^{90}Sr in milk?
- Are there any other facts they know about strontium in milk that may be included in the APS description?

Collection procedure:

- How preserved until analysis, type of cow, sheep, or goat matter?, Where they grazed?

Analytical Protocol Specifications

Analyte List: _____⁹⁰Sr_____

Analysis Limitations: _Perform direct measurement of analyte. Analysis of progeny allowed if radioactive equilibrium is established at laboratory from freshly isolated parent._

Matrix:__Raw Milk_____

Possible Interferences: Fresh beta-emitting, fission-product nuclides if purification steps are inadequate or non-existent.

Concentration Range: 1 to 50 pCi/L   **Action Level:_____ 8 pCi/L___**

Method Validation Level: MARLAP Levels A, C, or D as applicable. See Attachment C for details.

MQOs: __A required method uncertainty (u_{MR}) of 0.5 pCi/L or less at 8 pCi/L_____

Refer to the APS in the handout (Tab 14).

The questions that this segment of the APS answers are:

1. What? Radionuclide   Note: Only one analyte is listed. Exception would be gamma spectrometry.

2. Where? Matrix.   Note: Only one matrix is listed

3. How much? Upper/lower concentration range expected

4. Important level for decision making? Action level and required method uncertainty at the action level

5. How to prove it can be done? Method validation level (to be discussed during Module 9 on MARLAP Chapter 6)

6. Potential problems? Limits on the analysis and interferences. Heads up to the laboratory on what is needed to be accounted by the laboratory for the chemical separations and analyses.

MQO: A required method uncertainty (u_{MR}) of 0.5 pCi/L or less at 8 pCi/L

	LSC	Beta Detector	GPC	Required for Project
Routine Method Uncertainty (pCi/L)	0.2	1.0	0.3	0.5 (Required Method Uncertainty)

The TEC and radiochemical specialist need to asses the three methods and their method validation documentation, and determine which methods meet the APS specifications.

It should be emphasized that u_{MR} is one sigma (1σ).

LSC is liquid scintillation counter, GPC is gas proportional counting.

Stipulation of Quality Control

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

*Spiking range provided in Attachment B of the APS (Analyte Detection)

Refer to the APS in the handout (Tab 14, page 3).

These will be discussed in detail when we discuss Chapter 7. The Important points to note here are that the Project Manager decides the type of QCs to be performed and the frequency. This is an <u>example</u> of batch requirements for quality control samples!

ACTIVITIES	SPECIAL REQUIREMENTS
1. Field Sample Preparation/ Preservation	
2. Sample Receipt/Inspection	**See Example APS at Tab 14**
3. Lab Sample Preparation	

Continued...

This is an <u>example</u> APS. Refer to the APS in the handout (Tab 14, page 2).

ACTIVITIES	SPECIAL REQUIREMENTS
4. Sample Dissolution	
5. Chemical Separations	
6. Preparing Sources for Counting	
7. Nuclear Counting	See Example APS at Tab 14
8. Data Reduction and Reporting	
9. Sample Tracking Requirements	
10. Other- Chemical Yielding	

This is an example APS. Refer to the APS in the handout (Tab 14, page 2).

- Sample dissolution: NONE is listed. Does that mean that digestion *can't* be done? Remember, *performance-based requirements.*

- What is the significance of the chemical yield requirements being distinct for ^{85}Sr tracer *vs* Sr carrier? Minimize uncertainty due to yield mass, which ultimately minimizes uncertainty in the yield and the counting data.

1. Calculation methodology for ^{90}Sr
2. Combined standard uncertainty for ^{90}Sr calculation
3. Sample-specific MDC based on analytical parameters measured
4. Sample Specific critical level
5. Specific intermediate calculations required (ingrowth factors)
6. Data reduction process reviewed as on-site audit or desk audit, by client
7. No changes in data reduction process without approval

Continued...

<u>See Attachment A of APS at Tab 14, page 2</u>

NOTE **that these are examples of what could be requested by the client.**

*   Item 3 specifically discusses the MDC is a *sample* minimum detectable concentration vs a **method** minimum detectable concentration. NOTE: Item 3 does not discuss the use of a Yttrium yield. Is this an oversight, is a Y yield necessary?
*   Item 4 says that the critical level will be per individual sample.
*   Item 5 requires that the analytical laboratory report include the calculation steps for each sample with the sample's specific parameters used for each calculation.

1. Sample specific parameters to be reported
2. Sample processing factors or parameters
3. Required calculated information
4. Batch QC results to be reported with each batch of samples
5. Laboratory to provide a narrative for each batch of samples
6. Reports – electronically and as hard copy

See Attachment A of APS at Tab 14, page 2

These are examples of what could be requested by the client. There are additional factors that could be requested, such as:

- Certificates for standards used
- Trend graphs for all QC results
- Trend graphs for specific analyte recoveries
- Copies of "condition reports" or laboratory incident reports that may affect the sample processing
- Etc.

APS Documents the Key Analytical Planning Issues:

✓ Developed by the project team

✓ Created **before** sampling and analysis begin

✓ Tells the laboratory what is required of them in specific detail

✓ Identifies MQOs

✓ Used as the roadmap to validate/assess results

Because the APS documents the resolution of the key analytical planning issues:

- It is critical that the whole project team review the APS to ensure that the projected results will meet their specific needs.

- The APS must be done before anything is analyzed.

- There should be "give and take" with the laboratory so that the requirements in the APS are not overly restrictive.

- The MQOs should have already been selected and approved by all stakeholders, so that when results begin to accumulate there is no question as to what the measurements really mean.

- The data validators/verifiers and assessors should use the APS to ensure that the results have met the projected needs of the project.

MARLAP Recommends...

- Assumptions made during resolution of key analytical planning issues be documented
- Each radionuclide has an action level and a gray region
- MQOs be established for select method performance characteristics
- An MQO for method uncertainty always be established for each analyte/matrix combination
- That all measurement results be reported directly as obtained including negative values along with the measurement uncertainty

See handout of consolidated MARLAP recommendations for Part I (Tab 16).

- Each group will write their own APSs
- Each group will designate
  - Project Manager
  - Radiochemical specialist
  - Field sampling coordinator
  - Certified Health Physicist
- Blank APS form provided
- APSs will be based on "The Plutonium Fabricators, Ltd." scenario
- Solution will be distributed following exercise

The Project Planning Team usually consists of a project manager, one or more radioanalytical specialists, a certified health physicist, and a field sampling coordinator. MARLAP recommends that the composition and size of the team reflect the size and complexity of the project. The following are examples of project roles and responsibilities; they may change depending on the individual project:

- Certified Health Physicist: Responsible for dose assessment, field sampling Locations and modeling.

- Radiochemical specialist: Responsible for establishing the correct procedures for the analysis desired, the method uncertainty and data review and validation.

- Field sampling coordinator: Responsible for identifying the proper sampling techniques and validity of the samples.

- Turn to Tab 18.

Project Plan Documents: Important Recommendations

Module 5

David McCurdy

- Support data defensibility for environmental compliance
- Define project objectives
- Tool for communication with stakeholders

5. Project Plan Documents   2

- State the references used to support the data to be gathered (why we're doing ^{60}Co and not ^{55}Fe)
- Define and uphold the plan objectives — keep the project team focused.
- The stakeholders know what you're going to do

- Diversity of environmental data collection activities
  - Affects detail and content of plan
- Flexibility in applying guidance
  - According to the nature of the work being performed and the intended use of the data

MARLAP recommends that the project plan documents integrate all technical and quality aspects for the life cycle of the project

- Planning
- Implementation
- Assessment

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- Primary project plan document integrates the multi-disciplinary sections, other management plans, and stand-alone documents

- Appropriate management plans
  - Health and safety plan
  - Waste management plan
  - Risk analysis plan

Appropriate management plans may include these others as well:
- Community Relations Plan
- Records Management Plan
- If available, the data validation plan and DQA plan
- Detailed discussion of the project and a brief description of site history

Reasons Why:

- Federal and state agencies have different requirements for the various environmental data collection activities
- May be regulatory requirements
- Project plan document should reflect (and be consistent with) organization's QA policies and procedures

For example:
- Radiological Environmental Monitoring Program
- License Termination Plan
- Decontamination and Decommissioning, etc.

- ASTM D5283, Standard Practice for Generation of Environmental Data Related to Waste Management Activities: Quality Assurance and Quality Control Planning and Implementation

- ASTM D5612, Standard Guide for Quality Planning and Field Implementation of a Water Quality Measurements Program

- ASTM PS85, Standard Provisional Guidance for Expedited Site Characterization of Hazardous Waste Contaminated Sites

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- Project DQOs, APSs including the MQOs [Chapter 3]
- Sampling and analytical protocols that will achieve the project objectives [Chapters 3 and 10]
- Assessment procedures and documentation sufficient to confirm that the data are of the type and quality needed [Chapter 8]

Content of Project Plan Documents (4.5.1)

- Project description and objectives
- Identification of those involved in the data collection and their responsibilities and authorities
- Enumeration of the QC procedures to be followed
- Reference to specific SOPs that will be followed for all aspects of the projects
- Health and safety protocols

MARLAP *strongly discourages* using stand-alone plan components of equivalent status without integrating information and without a document being identified as a primary document [4.5.2]

MARLAP *recommends* using a formal process to control and document changes if updates of the original project plan document are needed. [4.6]

A. Project Management
- 9 elements

B. Measurement/Data Acquisition
- 10 elements

C. Assessment/Oversight
- 2 elements

D. Data Validation and Usability
- 3 elements.

See Table 4.2 in handouts

Refer to Table 4.2 behind Tab 15

TABLE 4.2. Crosswalk Between Project Plan Document Elements and Directed Planning Process

ID	Project Plan Document Elements (QAPP-EPA, 2001)	Content Measurement / Data Acquisition	Directed Planning Process Input
B4	Analytical Methods Requirements	Identify analytical methods and procedures included needed materials, waste disposal and corrective actions	Project Plan team: - Identifies input to the decision (analyte, matrices, etc.) - Establishes the required method uncertainty - Specifies the optimum sampling and analytical design
B5	Quality Control Requirements	1) Describe QC procedures and associated acceptance criteria and corrective actions for each sampling and analytical technique 2) Define the type and frequency of QC samples should be defined along with the equations for calculating QC statistics	Project Plan team: - Establishes the required method uncertainty, which will drive QC acceptance criteria - Establishes the optimized analytical protocols and desired MQOs

See Table 4.2 in handouts (Tab 15)

MARLAP Recommends...

- Using a **graded approach** to project plan writing because of the diversity of environmental data collection activities
- Developing a **primary integrating project plan** that includes other documents by citation or as appendices
- Developing project plan documents that integrate all technical and quality aspects for the **life-cycle** of the project, including planning, implementation, and assessment
- Including the report on the **directed planning process** in the project plan documents (by citation or in an appendix)

- Including a **summary of the planning process** if the planning process was not documented in a report
  - Assumptions and decisions, action levels, DQO statement, and APSs (which include the established MQOs and any specific analytical process requirements)
- Using a **formal process to control and document changes** if updates of the original project plan document are needed

Measurement Uncertainty

Module 6

Keith McCroan

Overview

- Basic concepts (e.g., what is "uncertainty")
- Why uncertainty is important
- The role that uncertainty plays in MARLAP
- Traditional practices
- The GUM
- Causes of uncertainty
- MARLAP's recommendations

What Is Uncertainty?

- In general, "uncertainty" means a lack of complete knowledge about something of interest

- In metrology (the science of measurement) *uncertainty* usually means *uncertainty of measurement*, which has a more precise definition

Definition of Uncertainty

- "Parameter, associated with the result of a measurement, that characterizes the dispersion of the values that could reasonably be attributed to the measurand" – *International Vocabulary of Basic and General Terms in Metrology (VIM)*

- Examples might include:
    - Standard deviation
    - Multiple of a standard deviation
    - Half-width of interval with stated level of confidence

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- Associated with result of a measurement

  (Not with a measurement process or procedure)

- Measurement result and the uncertainty together allow one to place reasonable bounds on what the "true" value might be

Recall that MARLAP defines the "method uncertainty" as a performance characteristic of a measurement process.

Question for the Class

- If a lab reports that a sample of soil from a frequently used playground contains 110 pCi/g of ^{239}Pu, what actions if any would you recommend?
  - Insist that the lab report uncertainty of result
- If the uncertainty is 10 pCi/g, one might conclude the playground should be closed while more tests are performed
- If the uncertainty is 300 pCi/g, the result doesn't mean much

Importance of Uncertainty

If the result of a measurement is reported without some indication of its uncertainty, the result is useless for decision making

Traceability

Are your results supposed to be "traceable"? If so,
note that the concept of traceability is defined as —

"Property of the result of a measurement or the value of
a standard whereby it can be related to stated
references, usually national or international standards,
through an unbroken chain of comparisons *all having
stated uncertainties*" – VIM

See notes to slide 12 for reference to VIM.

Role of Uncertainty in MARLAP

- MARLAP's approach to method evaluation and selection uses criteria based on measurement uncertainty (and the derived concept of method uncertainty)
- Criteria for *evaluating a lab's performance* based on required method uncertainty
- Criteria for *evaluating internal laboratory QC* based on measurement uncertainty
- Criteria for *making decisions about the contents of an individual sample* based on measurement uncertainty

Traditional Practices

- Radiochemists have known about uncertainty for many years, but for most of that time there was no standard terminology or notation
- Often use the term "sigma" to mean an uncertainty expressed as a standard deviation
- Some use one sigma (1σ) , 2σ, or even 1.96σ
- Uncertainty often stated without any explanation, leaving data users to make their own assumptions

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Traditional Practices

- Incomplete uncertainty evaluations common
- Reported uncertainty might be only the "counting error"
  - It is one component of the total uncertainty
- Sometimes result might be reported with a relative uncertainty of only a fraction of 1 % (usually unrealistic)
- Sometimes you might even see 0 ± 0 pCi/L (bad!)

- *Guide to the Expression of Uncertainty in Measurement* (GUM)
  - Published in 1993 by ISO in the name of 7 international organizations
  - Presents terminology, notation, and methods for evaluating and expressing measurement uncertainty
- Promotes more complete uncertainty evaluations and comparability of uncertainty statements

- International Organization for Standardization (ISO). 1995. *Guide to the Expression of Uncertainty in Measurement.* ISO, Geneva, Switzerland.
- The ISO *Guide to the Expression of Uncertainty in Measurement*, or GUM, is available in U.S. ($25) and international ($92) editions. The editions contain the same material, differing only in decimal marker, spelling, and size. The ISO *International Vocabulary of Basic and General Terms in Metrology* (VIM), 1993, a companion document to the GUM, is available only in an international edition ($71). The U.S. edition of the GUM is: *American National Standard for Expressing Uncertainty—U.S. Guide to the Expression of Uncertainty in Measurement*, ANSI/NCSL Z540-2-1997.

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- MARLAP's primary recommendation regarding measurement uncertainty is to

    Follow the GUM

    - So we speak and write the same language about uncertainty
    - So we can interpret each other's results and uncertainty statements

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MARLAP and the GUM

- If you follow the GUM, you're following the most important part of MARLAP's guidance for evaluating and expressing uncertainty

- MARLAP goes further and applies the GUM to radiochemical measurements

- Most of additional guidance is intended to be helpful, not prescriptive

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Question for the Class

How can you comply substantially with MARLAP's guidance for evaluating and expressing uncertainty?

GUM

Metrology and Statistics

- What we're doing is called *metrology*, defined as the science of measurement

- Metrology ≠ statistics, although metrology uses statistical methods and terminology

- Metrology uses lots of approximations (with no apologies) and defines new terms and symbols that a statistician wouldn't recognize

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Results as Random Variables

- We consider the result of a measurement to be a *random variable*

- The result can vary if the measurement is repeated, but it should vary in a manner that can be described probabilistically

- Can discuss its probability distribution, mean, standard deviation, etc.

Standard Uncertainty

- When we talk about the uncertainty of a result, we'll usually mean the uncertainty expressed as a standard deviation

- GUM calls this a *standard uncertainty*

- Traditionally standard uncertainty often called a "one sigma" uncertainty

What Causes Uncertainty?

- One of the best-known sources of uncertainty is "counting statistics"
- A radiation counting measurement is based on the detection of radioactive emissions produced by atoms of radionuclides as they decay
- Radioactive decay is inherently random
- We can describe the probability that an atom will decay during a specified time interval, but we can't be 100 % certain

Counting Uncertainty

- Radiation detection can also be random

- If you could repeat the same radiation counting measurement over and over with the same initial conditions, you'd get a different result each time

- Uncertainty of a result due to the randomness of radioactive decay and radiation detection is what MARLAP calls the *counting uncertainty*

Causes of Uncertainty: Subsampling

- Often the lab analyzes only a small portion of a much larger sample
- A typical sample has some heterogeneity, so one portion differs in composition from another
- Uncertainty due to subsampling is potentially very large, but may be hard to quantify

Causes of Uncertainty: Instruments

- Measuring instruments and their operators aren't perfect
- Radiation detectors usually aren't capable of detecting every particle or ray emitted from the sample
- Even volumes obtained using volumetric glassware and masses measured using precise analytical balances have uncertainty

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Causes of Uncertainty: Standards

- Standards have uncertainties in their stated values
  - Including standard solutions used for instrument calibration
- Typical (standard) uncertainty for standard solution is ~ 0.5 % to 2 %
- These uncertainties may exceed the uncertainty due to counting statistics for measurements of samples with very high levels of activity

Causes of Uncertainty: Other

- Many other causes of uncertainty
  - Variable background radiation levels (e.g., cosmic)
  - Errors in mathematical models used to describe measurement process (e.g., calibration curves)
  - Errors in published values for constants (e.g., half-lives and radiation-emission probabilities)
  - Impurities in reagents
  - Contamination of glassware or instruments
  - Changing environmental conditions in the lab (temperature and humidity)

Uncertainty Propagation

- Final result typically not measured directly but calculated from other measured values

- Measured values might include volumes, masses, times, and numbers of counts

- Uncertainties of the input values combine to produce uncertainty in output value

- Mathematical operation of combining individual uncertainties to obtain the total uncertainty of final result is called *propagation* of uncertainty

Combined Standard Uncertainty

- Standard uncertainty of a result obtained by propagating the standard uncertainties of all the input values is called the *combined standard uncertainty*

- "Total propagated uncertainty" (TPU) previously used to denote same concept

GUM

- Standard uncertainty denoted by lower-case u
- If x is a measured value, standard uncertainty is $u(x)$
- *Exception*: If standard uncertainty is *combined* standard uncertainty, it may be denoted by $u_c(x)$
- Expanded uncertainty denoted by upper-case U

incompletely defined

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- Propagating uncertainty not the simple addition of uncertainty components
- If you multiply a result x by a constant c, the standard uncertainty of the product is $|c| \times u(x)$
- If you add two values x and y, the standard uncertainty of their sum is the square root of the sum of the squares of $u(x)$ and $u(y)$

$$u(x + y) = \sqrt{u^2(x) + u^2(y)}$$

  - Think of the Pythagorean Theorem (next slide)
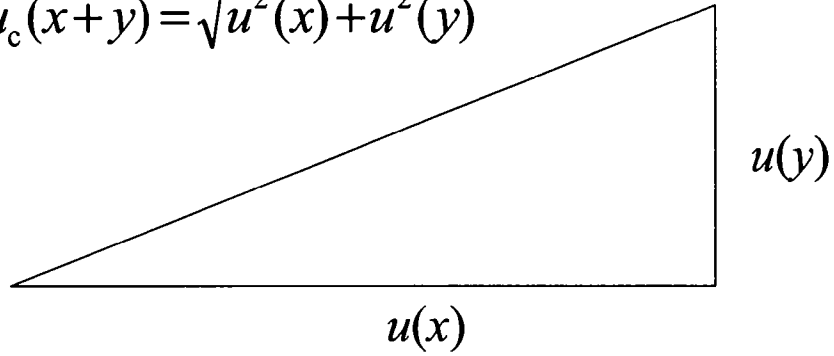
- A consequence of rules for uncertainty propagation:
  - Small uncertainty components tend to contribute even less to the total uncertainty than one might think
- Combine two uncertainty components 10 and 3 – the total uncertainty is only 10.4, not 13

an RMS value

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Expanded Uncertainty

- The lab might report the combined standard uncertainty for each result...
- Or multiply CSU by k to obtain a larger uncertainty, obtaining a wider interval about the result with greater probability of containing the true value
- Product of $k \times$ CSU = *expanded uncertainty*
- Factor k called *coverage factor*

Questions for the Class

- What is standard uncertainty?

- What is combined standard uncertainty?

- How do you denote the combined standard uncertainty of y? $(S \cup$

  u_c / y

- What is expanded uncertainty? $= CS \cup \times |<$

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Rounding Results

- Consider a result reported as 15.381 pCi/g with CSU 4.076 pCi/g
- Final digits in the result don't mean much, because of the uncertainty
- More sensible to report the result as 15 with uncertainty of 4, or 15.4 with uncertainty of 4.1

Rounding Rules

- There is a widely accepted method for rounding results with uncertainty
- Regardless of whether you report the CSU or an expanded uncertainty, round the uncertainty to either 1 or 2 figures
  - MARLAP prefers 2 in all cases – Others may differ
- Then round the result to the same number of decimal places

- Suppose a measurement result is 17.93602 Bq/L, and lab reports the result with a CSU of 0.37301 Bq/L.
- How would you round the result and the CSU according to MARLAP?

$$17.93 \pm 0.37$$

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Shorthand Notations

- There are common shorthand notations for reporting uncertainty
- If reporting CSU, place the digits of the rounded uncertainty in parentheses just after the digits of the rounded result:

$$17.94(37) \text{ Bq/L}$$

- This format is not commonly used by radiochemists
- May be encountered in published documents

- For expanded uncertainty, report the numerical values of the result and uncertainty in parentheses followed by the unit of measurement, with the result and uncertainty separated by ± (or +−):

$$(17.94 \pm 0.75) \ Bq/L$$

- This format is more familiar to radiochemists

Explain the Uncertainty

- Even if you use an accepted shorthand notation, explain what it means

Always explain the uncertainty

- In particular state whether it is a CSU or an expanded uncertainty, and in the latter case, state the coverage factor

Summary of MARLAP's Recommendations

- Use the terminology, notation, and methodology of GUM

- Report all results – even if zero or negative – unless believe they are invalid

- Report either combined standard uncertainty or an expanded uncertainty for each result

- Explain the uncertainty – in particular, state coverage factor for an expanded uncertainty

(continued)

- Consider all sources of uncertainty, and evaluate and propagate all that are believed to be potentially significant in final result
- Do not ignore subsampling uncertainty (for solid samples) just because hard to evaluate
- Round reported uncertainty to 1 or 2 figures (we suggest 2) and round the result to match

Final Recommendation

- All preceding recommendations are severable
- Do as much as you can
- At least use GUM's terminology and notation so that we all speak and write the same language
- Make further progress as time and resources permit

Does MARLAP prefer that a lab report the combined standard uncertainty of each result, or an expanded uncertainty?

either /ur — 10/spec

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When a lab reports an expanded uncertainty, what coverage factor does MARLAP prefer?

none.

2 -3 common

What does the notation 12.34(56) Bq/g mean?

What does the notation (12.34 ± 0.56) Bq/g mean?

Exponent (?)

explain coverage factor

Your Questions?

Evaluating Measurement Uncertainty

Module 7

Keith McCroan

Overview

- Brief review of Module 6
- Uncertainty evaluation
  - How does one calculate and propagate uncertainty?
  - What are some pitfalls?
  - What tools are available to make it easier?
  - Some examples and one exercise

- What is MARLAP's primary recommendation regarding measurement uncertainty?

- What is a standard uncertainty?

- What is a combined standard uncertainty?

Review of Module 6

- What is expanded uncertainty?

- What is a coverage factor?

Mathematical model

- Typically one does not measure the final result directly
- The value is calculated from other measured values using a *mathematical model* of the measurement
- The model relates values of the directly measured quantities (*input quantities*) to the final result (*output quantity*, which is the *measurand*)

The Model

- Model might be a single equation or set of equations
- We follow the GUM here and represent it abstractly as a single equation

$$Y = f(X_1, X_2, \ldots, X_N)$$

Y denotes output quantity and $X_1, X_2, \ldots, X_N$ denote input quantities

We use upper-case variables for the input quantities and output quantities (when we write the model abstractly).

Input Estimates

- Given a mathematical model of the measurement, making a measurement requires estimating values of the input quantities and using them to calculate the value of the output quantity
- Estimated values of the input quantities are called *input estimates*
- We denote input estimates as $x_1, x_2, \ldots, x_N$.

- Given the model and the input estimates, the value of the output quantity is calculated
- The calculated value is the *output estimate*:

$$y = f(x_1, x_2, \ldots, x_N)$$

We use lower-case variables for the input estimates and output estimate.

When you actually apply this theory, you'll use the same variable symbols whether you're talking about the quantity or the estimated value of the quantity.

Evaluating Uncertainty

- We want the combined standard uncertainty of the output estimate, y
- First need the standard uncertainty of each input estimate, x_i
- Then determine how much each of these uncertainties contributes to the total uncertainty of y
- Many ways to do the first step

(handwritten top:) > 1. cont

Methods of Uncertainty Evaluation

GUM describes two general types of uncertainty
evaluation (for input estimates)

– *Type A* evaluation of standard uncertainty: by
statistical analysis of series of observations

– *Type B* evaluation of standard uncertainty: by any
other means

(handwritten right:)) formerly "random"

) formerly "systematic"

(handwritten:) typed by the way you evaluate.

- Canonical example:
  - Series of replicate measurements of input quantity X_i
  - Estimate the value by the average of the results
  - Estimate the standard uncertainty by the *experimental standard deviation of the mean*
- Least-squares regression is also a Type A method
- If you have "degrees of freedom," it's probably a Type A method

Example: Type A evaluation

- Make 6 measurements of an input quantity, X_i:

  $x_{i,1}=12, x_{i,2}=9, x_{i,3}=12, x_{i,4}=10, x_{i,5}=11, x_{i,6}=9$

- Use average as input estimate:

  $x_i = (12+9+12+10+11+9) / 6 = 63 / 6 = 10.5$

- Experimental standard deviation* of these 6 values $s(x_{i,k}) = 1.378$

- Let $u(x_i)$ be the *experimental standard deviation of the mean*, which equals $1.378 / \sqrt{6} = 0.5627$

*See next slide

$$x_i = \bar{x}_i = \frac{1}{6}\sum_{k=1}^{6} x_{i,k} = \frac{12 + 9 + 12 + 10 + 11 + 9}{6} = \frac{63}{6} = 10.5$$

$$s(x_{i,k}) = \sqrt{\frac{1}{6-1}\sum_{k=1}^{6} (x_{i,k} - \bar{x}_i)^2}$$

$$= \sqrt{\frac{1}{5}\left((1.5)^2 + (-1.5)^2 + (1.5)^2 + (-0.5)^2 + (0.5)^2 + (-1.5)^2\right)}$$

$$= \sqrt{1.9}$$

$$= 1.378$$

$$u(x_i) = s(\bar{x}_i) = \frac{s(x_{i,k})}{\sqrt{6}} = \frac{1.378}{\sqrt{6}} = 0.5627$$

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typically based one one count

Type B evaluations

- Any method of uncertainty evaluation that isn't Type A is Type B
- Many Type B examples, including
  - Poisson counting uncertainty
  - Using tolerances
  - Importing values with uncertainties from other sources
- Sometimes a Type B evaluation is based on professional judgment
  - Don't be afraid to make an educated guess $\left(> \text{ignoring it} \right)$

In particular, if the uncertainty component is small, don't be afraid to guesstimate it.

E.g., how far might the meniscus deviate from the capacity mark in a pipet?

1st Example: Poisson counting

- Estimate standard uncertainty of the number of counts, N, observed in a typical radiation counting measurement by square root of N
- Assuming distribution of N is Poisson:
  - *Standard deviation = square root of the mean*

Example: Poisson counting

- Radiation-counting measurement where distribution assumed Poisson
  - Observe $N = 169$ counts
- Standard uncertainty evaluated to be $\sqrt{169} = 13$

- One may see results reported as 0 ± 0
  - When blank (or background) count and sample count are zero and counting uncertainty is estimated by taking square root of the count
- Reporting 0 ± 0 or anything ± 0 is a bad idea
- MARLAP recommends that when very low numbers of counts possible, evaluate uncertainty of N as

$$u(N) = \sqrt{N+1}$$

Example: Low-level Poisson

- Suppose sample count, N_s, happens to be 1
- Evaluate the uncertainty of N_s by

$$u(N_s) = \sqrt{N_s + 1} = \sqrt{1+1} = \sqrt{2} = 1.414$$

2nd Example: Rounding

- Suppose an input estimate is rounded to 0.8
- The original value might have been between 0.75 and 0.85
- How to account for this uncertainty?
- Assume a *rectangular distribution** centered on 0.8, with *half-width* $a = 0.05$
- Divide half-width a by $\sqrt{3}$ to get standard uncertainty of the input estimate   *value because it's rectangular*

* See next slide

7. Evaluating Measurement Uncertainty   19

When you round a measured result, you lose information and increase uncertainty.

But when done properly, rounding should add negligible uncertainty.

$$u(x_i) = \frac{a}{\sqrt{3}}$$

$\leftarrow u(x_i) \rightarrow$

$x_i - a$ $\qquad$ x_i $\qquad$ $x_i + a$
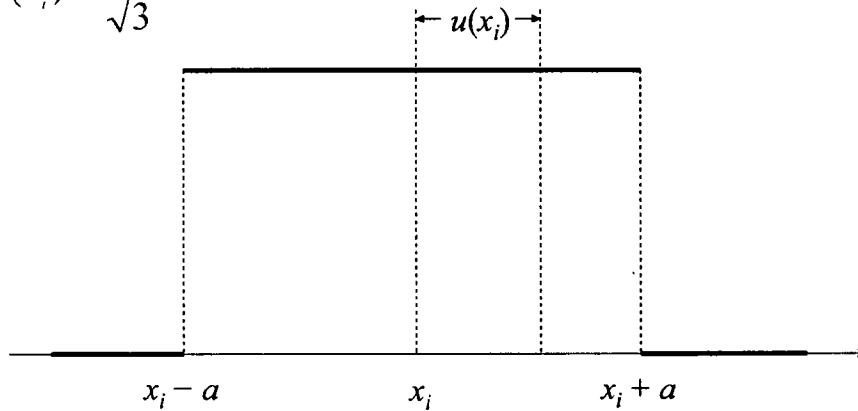
The rectangular distribution assumes values between the lower and upper bound are equally likely, and no other values are possible.

3rd Example: Capacity of Pipet

- There is uncertainty in the capacity of a volumetric pipet
- ASTM class A volumetric pipet has a stated tolerance a for the nominal capacity V
- Any value between $V - a$ and $V + a$ is possible, but assume values near V are most likely
- Assume a *triangular distribution**, centered on V, with half-width a
- Divide half-width a by $\sqrt{6}$ to get standard uncertainty of V

See next slide

The triangular distribution assumes that only values between the lower and upper bound are possible, but values near the center are most likely.

Example: Triangular

- Suppose the nominal capacity, V, of an ASTM class A volumetric pipet is 1 mL with a specified tolerance of $a = 0.006$ mL

- Assume a triangular distribution for the error and calculate the standard uncertainty of V

$$u(V) = a / \sqrt{6} = 0.006 \text{ mL} / 2.4495 = 0.00245 \text{ mL}$$

Note

- Uncertainty of pipet's capacity is not the total uncertainty of volume delivered
- Total uncertainty depends on operator's skill (among other things)
- However, the uncertainty does tend to be relatively small

In many rad-chem measurements, the uncertainty of pipetting is one of the least of your concerns.

Balance measurements also tend to have very small uncertainty when performed properly.

- Rectangular and triangular distributions are often used when you can estimate a bound *a* for the largest possible error in your estimate
- If you know nothing else about the distribution of the error, assume a *rectangular* distribution
- If you think values near your estimate are more likely than values near the bounds, assume a *triangular* distribution

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4th Example: Imported values

- If you *import* a value measured by someone else (e.g., a half-life measured by NNDC) and use the reported uncertainty, that's a Type B evaluation
- If you buy a standard with a stated value and a confidence interval (say 95 %), divide the half-width of the confidence interval by an appropriate percentile of the standard normal distribution to get the standard uncertainty

- Suppose the stated massic activity for a standard solution is 204.1 Bq/g with 95 % confidence limits at ±3.2 Bq/g.
- What is the standard uncertainty of the massic activity?

dividing by ν

Divide 3.2 Bq/g by 1.960 (97.5th percentile of the standard normal distribution) to get the standard uncertainty, 1.6 Bq/g

- For a typical measurement process, one calculates the final result using a mathematical model of the measurement

$$Y = f(X_1, X_2, \ldots, X_N)$$

- Measure or import estimates $x_1, x_2, \ldots, x_N$ of the input quantities and calculate an estimate y for the output quantity

$$y = f(x_1, x_2, \ldots, x_N)$$

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Uncertainty Propagation

- Use same model to determine how standard uncertainties of input estimates, $x_1, x_2, \ldots, x_N$, produce combined standard uncertainty of the output estimate, y

- Mathematical operation of combining uncertainties of the input estimates to get the uncertainty of the output estimate is called *propagation of uncertainty*

How Uncertainties Combine

- Suppose $u(x_1) = 1.5$ and $u(x_2) = 2$
- What is the uncertainty of the sum $x_1 + x_2$?
- Uncertainties generally add "in quadrature"
  - Square each uncertainty, add the squares, and take the square root of the sum
- Answer in this case is not $1.5 + 2 = 3.5$, but

$$\sqrt{2.25 + 4} = 2.5$$

always sq root (not nth root)

Components of Uncertainty

- If model is more complicated than a simple sum, think in terms of uncertainty "components"
- An uncertainty *component* is the part of the total uncertainty of y that is generated by just one input estimate x_i
- Uncertainty propagation usually consists of calculating all the uncertainty components, squaring them, adding up their squares, and then taking the square root of the sum

Sensitivity

- Uncertainty component due to x_i depends on the uncertainty $u(x_i)$ and also on how sensitive y is to changes in x_i

- If large errors in x_i don't generate large errors in y, then y is not very "sensitive" to x_i

- Might be a large uncertainty in the time of sample collection, but the sensitivity of the decay-correction factor depends on the half-life (e.g., ^{131}I vs ^{238}U)

- The *component* of the combined standard uncertainty $u_c(y)$ generated by $u(x_i)$ is:

a partial derivative

$$u_i(y) = \left| \frac{\partial f}{\partial x_i} \right| \times u(x_i)$$

- $\partial f / \partial x_i$ is a *sensitivity coefficient* because it indicates how "sensitive" y is to changes (or errors) in the value of x_i

Estimating Uncertainty Components

- Generally preferred that sensitivity coefficients be calculated using rules of calculus
- But it is also OK to estimate the sensitivity coefficients or the uncertainty components (e.g., spreadsheet methods)
- One way to estimate an uncertainty component without calculus is:

$$u_i(y) \approx \frac{1}{2}\left|f(x_1,...,x_i+u(x_i),...,x_N) - f(x_1,...,x_i-u(x_i),...,x_N)\right|$$

Change a value f to est ?ns

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- Equation for propagating uncertainty can be written in two ways

$$u_c(y) = \sqrt{\sum_{i=1}^{N} u_i^2(y)} = \sqrt{\sum_{i=1}^{N} \left(\frac{\partial f}{\partial x_i}\right)^2 u^2(x_i)}$$

- GUM calls this equation the *law of propagation of uncertainty*

- MARLAP prefers the less grandiose name *uncertainty propagation formula*

Derivatives

- $\partial f / \partial x_i$ indicates how much y changes when x_i changes by a small amount
- E.g., if $y = 2x_1 - 4x_2$, then $\partial f / \partial x_1 = 2$ and $\partial f / \partial x_2 = -4$
- For more complicated functions, you need calculus (or estimation procedures)

- Simple model $y = 2x_1 - 4x_2$

  where $u(x_1) = 1.5$ and $u(x_2) = 1.0$
- $u_1(y) = |2| \times u(x_1) = 2 \times 1.5 = 3.0$
- $u_2(y) = |-4| \times u(x_2) = 4 \times 1.0 = 4.0$

$$u_c(y) = \sqrt{3.0^2 + 4.0^2} = \sqrt{25.0} = 5.0$$

Graphical Uncertainty Propagation

$y = 2x_1 - 4x_2$

$u(x_1) = 1.5$

$u(x_2) = 1.0$

$u_1(y) = 2 \times 1.5 = 3.0$

$u_2(y) = 4 \times 1.0 = 4.0$

$u_c(y) = \sqrt{u_1^2(y) + u_2^2(y)}$

Comb uncert.

$u_c(y) = 5.0$

$u_2(y) = 4.0$

2nd component

$u_1(y) = 3.0$
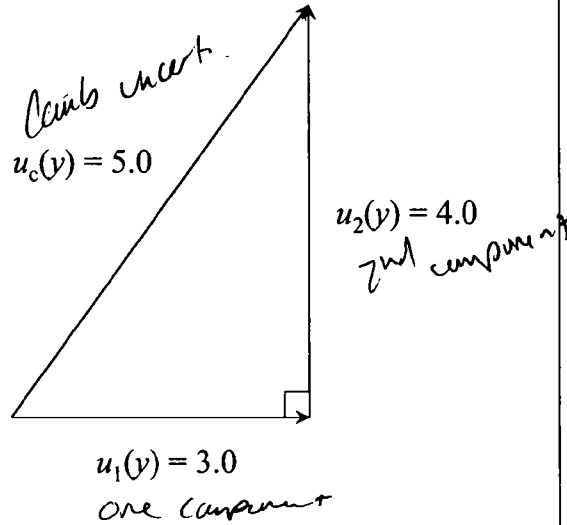
One Component

Here is the same example illustrated with a diagram.

If the model involves only 2 inputs, the uncertainty components combine in the manner shown here.

The length of the blue line indicates the combined standard uncertainty.

Remember the Pythagorean Theorem.

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- Small uncertainty component has even less impact on the total uncertainty than one might think

- In example below, $u_c(y)$ is almost identical to the larger component, $u_1(y)$

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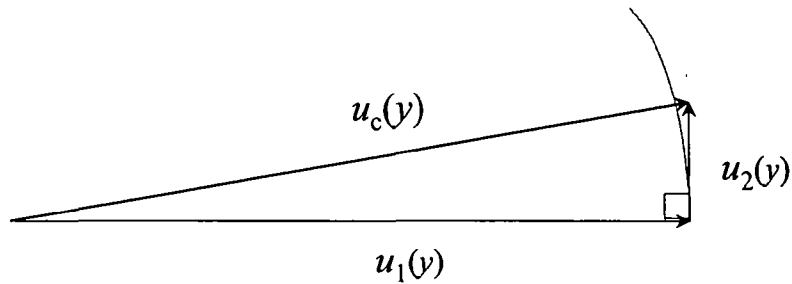
not independent

- The form of the uncertainty propagation formula shown earlier assumes that all the input estimates are determined independently of each other

- If some pairs of input estimates are correlated with each other, you need a different version of the formula

$$u_c(y) = \sqrt{\sum_{i=1}^{N}\left(\frac{\partial f}{\partial x_i}\right)^2 u^2(x_i) + 2\sum_{i=1}^{N-1}\sum_{j=i+1}^{N}\frac{\partial f}{\partial x_i}\frac{\partial f}{\partial x_j}u(x_i, x_j)}$$

extra term to account for covariance

7. Evaluating Measurement Uncertainty   40

Earlier we didn't tell you the whole truth about uncertainty propagation. Sometimes there are complications.

What Causes Correlations?

- Two or more inputs in the model might be calculated from the same data (e.g., parameters for a calibration curve estimated by least squares)
- Physics (e.g., the areas of two photopeaks in a gamma spectrum might be correlated)
- Environmental influences (e.g., temperature and humidity) but often too small to care about

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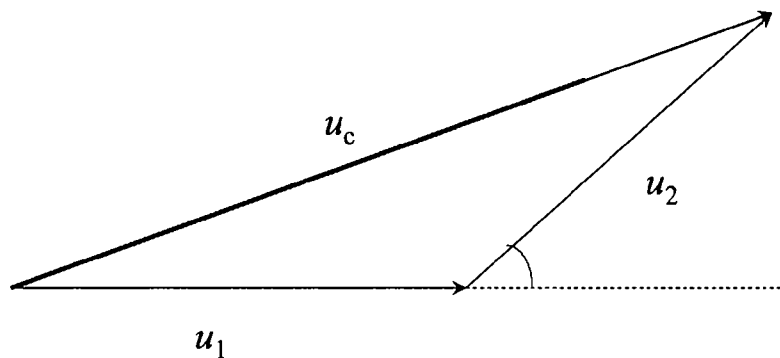
Depending on the signs of the correlation coefficient $r(x_1,x_2)$ and sensitivity coefficients $\partial f / \partial x_1$ and $\partial f / \partial x_2$, a correlation might either increase or decrease the combined standard uncertainty. On this slide we see an increase.

The value of the correlation coefficient $r(x_1,x_2)$ is related to the cosine of the angle you see marked on the slide. (It has the same magnitude but perhaps a different sign.)

The length of the blue line segment shows the magnitude of u_c.

For comparison, the red line segment shows the magnitude of u_c if the correlation coefficient were zero.
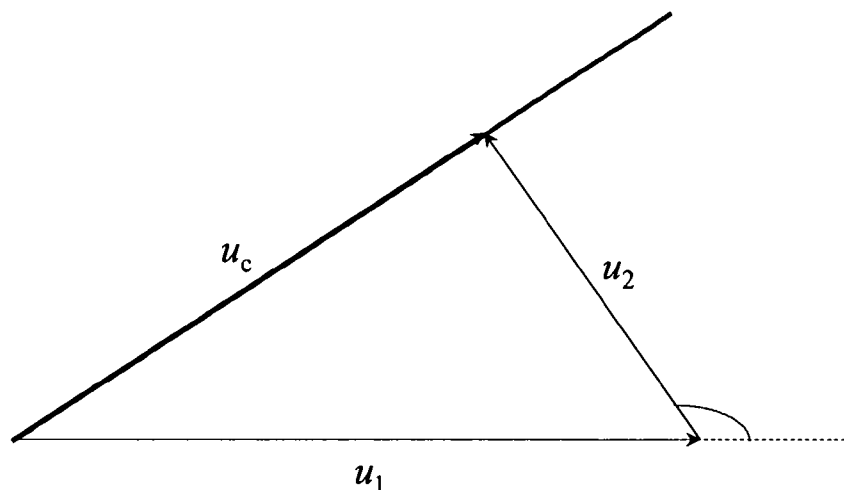
On this slide we see a situation where the effect of the correlation is to make the combined standard uncertainty smaller than it otherwise would have been.

Again, the value of the correlation coefficient for x_1 and x_2 is related to the cosine of the angle you see marked.

The length of the blue line segment shows the magnitude of u_c.

For comparison, the red line segment shows the magnitude of u_c if the correlation coefficient were zero.

How to Estimate Correlations

- Experimentally
  - Type A evaluation of covariance based on a series of paired measurements of two quantities
- Calculate covariance using a formula similar to the uncertainty propagation formula
- See MARLAP Chapter 19 for more details

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- It helps to remember shortcut formulas for propagating uncertainty
- For example, if all the input estimates $x_1, \ldots, x_K$, and $z_1, \ldots, z_L$ are nonzero and uncorrelated, and if

$$y = \frac{x_1 \times \cdots \times x_K}{z_1 \times \cdots \times z_L}$$

then

$$u_c(y) = \sqrt{y^2 \times \left(\frac{u^2(x_1)}{x_1^2} + \cdots + \frac{u^2(x_K)}{x_K^2} + \frac{u^2(z_1)}{z_1^2} + \cdots + \frac{u^2(z_L)}{z_L^2} \right)}$$

What happens if x_i is zero?

What happens if z_j is zero?

- In radiochemistry, the following type of model is common:

$$y = \frac{R_{net}}{\varepsilon \times Y \times V} \quad \frac{\textit{net count rate}}{\textit{count eff} \cdot \textit{yield} \cdot \textit{volume}}.$$

- The uncertainty equation for y can be written as follows (if no correlations):

$$u_c(y) = \sqrt{\frac{u_c^2(R_{net})}{\varepsilon^2 \times Y^2 \times V^2} + y^2 \times \left(\frac{u^2(\varepsilon)}{\varepsilon^2} + \frac{u^2(Y)}{Y^2} + \frac{u^2(V)}{V^2} \right)}$$

The numerator is a net count rate. The denominator is a product of factors: detection efficiency, chemical yield, sample volume analyzed.

This paradigm works for any number of factors in the denominator. So, you could include decay/ingrowth factor (D) and emission probability (P) too.

Pitfalls of Uncertainty Evaluation

Pitfall #1

- Sometimes one input quantity appears in the mathematical model more than once
- What's the problem?
- You might be tempted to treat each occurrence of the variable as if it were a distinct variable
- Think about it. What is the uncertainty of $x - x$?

  It isn't $\sqrt{u^2(x)+u^2(x)}$
- It's *zero*

Note that $x - x$ is an artificial example, which you probably will never encounter in practice.

But obviously, the value of $x - x$ is exactly zero, with no uncertainty, even if the value of x is uncertain.

Example: Repeated Variables

- Here's a real example encountered not long ago
- How to calculate uncertainty of

$$y = \frac{x_1}{x_1 + x_2}$$

- Does the uncertainty of x_1 contribute more uncertainty to y because x_1 appears twice?
- If you say YES, then what is the uncertainty of the following?

$$z = 1 - y = \frac{x_2}{x_1 + x_2}$$

In the real world, the x's were numbers of counts, and y was a kind of "spillover" factor.

- Both y and z must have exactly the same uncertainty

$$\frac{\partial y}{\partial x_1} = \frac{x_2}{(x_1 + x_2)^2} = -\frac{\partial z}{\partial x_1}$$

$$\frac{\partial y}{\partial x_2} = \frac{-x_1}{(x_1 + x_2)^2} = -\frac{\partial z}{\partial x_2}$$

$$u_c^2(y) = \left(\frac{x_2}{(x_1 + x_2)^2}\right)^2 u^2(x_1) + \left(\frac{-x_1}{(x_1 + x_2)^2}\right)^2 u^2(x_2)$$

$$= \frac{x_2^2 u^2(x_1) + x_1^2 u^2(x_2)}{(x_1 + x_2)^4}$$

Since $z = 1 - y$, and the 1 has no uncertainty, it follows that $u(z) = u(y)$.

Pitfalls of Uncertainty Evaluation (Continued)

Pitfall #1 (continued)

- Sometimes variables that appear explicitly in the model might be calculated from other variables
- Could tend to obscure fact that some variables (in effect) appear twice in the model
- Good example of this in alpha spectrometry using a tracer, where detection efficiency is used in the calculation of the yield
- Efficiency actually has no effect on the final result (cancels out)

Pitfall #2

- Beware of some shortcut formulas when the output estimate is zero
- Remember

$$y = \frac{R_{net}}{\varepsilon \times Y \times V}$$

$$u_c(y) = \sqrt{\frac{u_c^2(R_{net})}{\varepsilon^2 \times Y^2 \times V^2} + y^2 \times \left(\frac{u^2(\varepsilon)}{\varepsilon^2} + \frac{u^2(Y)}{Y^2} + \frac{u^2(V)}{V^2}\right)}$$

- Not

$$u_c(y) = \sqrt{y^2 \times \left(\frac{u_c^2(R_{net})}{R_{net}^2} + \frac{u^2(\varepsilon)}{\varepsilon^2} + \frac{u^2(Y)}{Y^2} + \frac{u^2(V)}{V^2}\right)}$$

If the net count rate, R_{net}, is zero, the latter uncertainty equation causes a divide-by-zero error, or, if you avoid that error, you calculate zero for the uncertainty of y. Either way, you make a mistake.

$\text{Sometimes} = \emptyset$

Pitfalls of Uncertainty Evaluation (Continued)

Pitfall #3

- Everyone likes to assume Poisson counting statistics and estimate the counting uncertainty by $\sqrt{N}$
- What's wrong with that?
- Often nothing, but when counting combined emissions from more than one nuclide in a short-lived decay chain, Poisson model isn't valid
  - Generally underestimates the uncertainty
- Deviation from Poisson is greater when detection efficiency is high

Example: ^{222}Rn in a Scintillation Cell

- Classic example is counting ^{222}Rn and progeny in alpha scintillation cell (Lucas cell)
- Get alpha counts from ^{222}Rn, ^{218}Po, and ^{214}Po
- Detection efficiency is usually high
- Counts tend to occur in clusters as one atom decays through several states, not as independent events
- Described by H.F. Lucas in the early 1960s but still widely unknown

Other Examples of Non-Poisson Counting

- Beta-counting ^{234}Th, which has the short-lived decay product, ^{234m}Pa, another beta-emitter
- Any gross counting measurement where the nuclides are unknown
  - Gross alpha, gross beta, gross gamma

Gross beta in particular often has a high detection efficiency.

Gamma-ray detection efficiency is often low, so Poisson model may be OK.

Pitfall #4

- Some sources of uncertainty not shown explicitly in the model
- E.g., variability in the instrument background, or varying levels of contamination in the blank
  - Include explicit extra term in the model or increase the uncertainty of the blank count
- Error due to subsampling heterogeneous solid material, such as soil or sediment
  - See MARLAP Chapter 19 and Appendix F

Pitfall #5

- If model is nonlinear and some input estimates have large uncertainties, uncertainty propagation formula may not work

- Uncertainty propagation formula based on an approximation, which may not always be adequate

- As a rule, keep relative uncertainties of count times, aliquant sizes, decay-correction factors, detection efficiencies, and yields small

- Uncertainties of the raw counts can usually be large (except for the tracer count)

Software Tools

- Software tools make uncertainty evaluations easier
- Kragten spreadsheet method can be used by anyone with a spreadsheet program
- Standalone software systems (some free) and software component libraries that do uncertainty propagation automatically

7. Evaluating Measurement Uncertainty   57

References: www.Measurement uncerta ih . org

- Kragten, J. 1994. "Calculating standard deviations and confidence intervals with a universally applicable spreadsheet technique," *Analyst*, 119(10), pp. 2161–2166.

- Vetter, Thomas W. 2001. "Quantifying Measurement Uncertainty In Analytical Chemistry – A Simplified Practical Approach." National Institute of Standards and Technology (NIST), Gaithersburg, MD 20899-8393. Available at http://www.cstl.nist.gov/div839/839.03/Uncertainty.pdf.

Vetter's online article describes the Kragten technique and applies it to analytical chemistry.

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GumCalc

- *GumCalc*: free standalone software system developed to support MARLAP
- Allows you to define a mathematical model of a measurement, specify uncertainties of the input estimates, and propagate uncertainty automatically
- Propagates dimensions of quantities and does unit conversions
- Imports raw data and exports results to CSV files
- Available at www.mccroan.com/GumCalc.htm

- Another source of free software for uncertainty propagation is http://metrologyforum.tm.agilent.com/download3.shtml

- The GUM Workbench is available (for purchase) at: http://www.gum.dk/e-wb-home/gw_home.html

Mention of trade names or specific applications does not imply endorsement or acceptance by the U.S Environmental Protection Agency or any MARLAP agency.

Parting Thoughts

- Many people focus on uncertainty propagation as the difficult problem that prevents better uncertainty evaluations
- The uncertainty propagation formula looks complicated because of summation symbols and partial derivatives
- Actually straightforward – can be implemented automatically by reusable software components

Continued...

- What's hard about uncertainty evaluation is not propagation of uncertainty but understanding the measurement process well enough to know what uncertainties need to be propagated

- Software won't solve this problem for you anytime soon

Class Exercise

Questions?

Obtaining Laboratory Services

Module 8

Dave McCurdy

Appendix E: *Contracting Laboratory Services*

- More extensive than Chapter 5
- Provides detailed information
- Covers multi-agency contracting vehicles

Appendix E:

- Request for Proposals (the solicitation)
- Proposal requirements
- Proposal evaluation and scoring procedures
- The award
- Duration of contract (period of performance and milestones)
- Contract completion

Contract Specifications...

- Capture analytical requirements in a concise ~~a At As~~ format

- Verify that project planning documents contain all the information required

- Identify laboratory's responsibility for documentation

- <u>Capture analytical requirements in a concise format</u>: facilitates selection of appropriate analytical protocols by laboratory
- <u>Verify that project planning documents contain all the information required</u>: selection and implementation of the appropriate analytical protocols
- <u>Identify laboratory's responsibility for documentation</u>: data verification, validation, and quality assessment

Procurement Cycle

Planning

Procurement Process — Includes SOW
Section E.2

Request for Proposals — Reflects SOW
Section E.3

Procurement Process
Section E.4

Review, Evaluate, Score, Audit
Section E.5

Award
Section E.6

Contractor Services
Section E 7

— Periodic Evaluations
Progress According to SOW

Contract Completion
Section E.8

6. Obtaining Laboratory Services
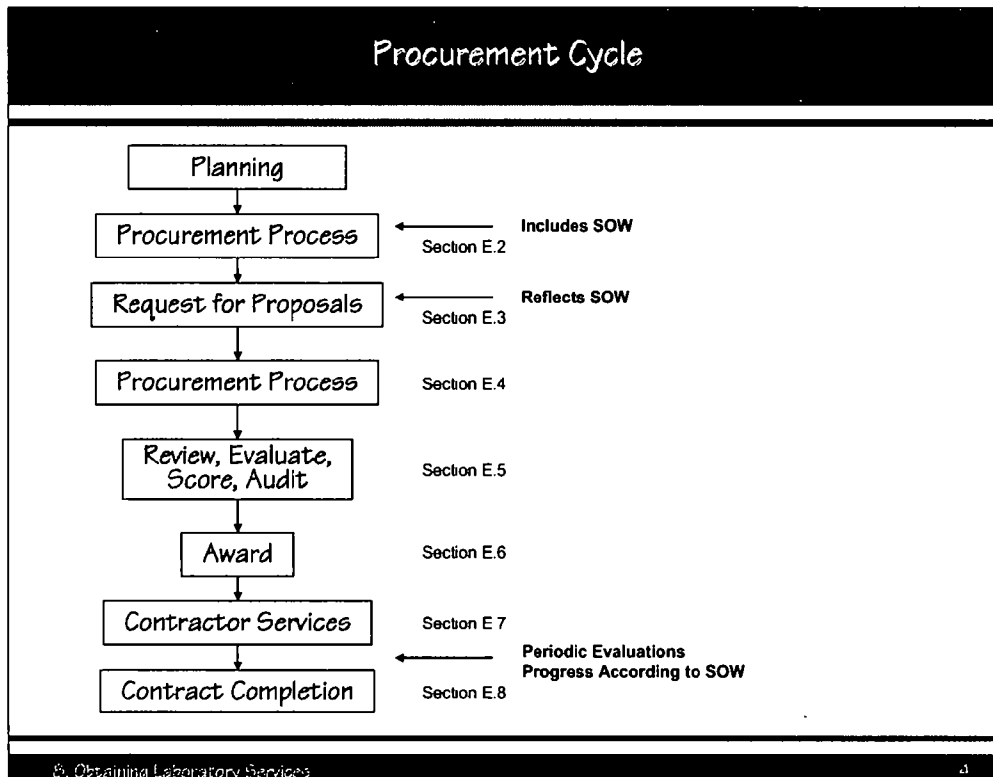
MARLAP's procurement discussions generally conform to the Federal Acquisition Regulations (FAR). FAR may not apply to states, universities, or private-sector purchasers, but most large organizations have comparable requirements and regulations.

4

- Purchase Order
- Noncompetetive procurements ("Sole Source") *(sole not nego)*
- Invitation for Bid (IFB) — *other u&l w/ BoA*
- Request for Quotation (RFQ) – *Sow not nego*

Continued...

Purchase Order
- In-house process handled through purchasing staff; usually has a not-to-exceed limit for purchasing
- Limited to small needs without a formal request; may be used to purchase a limited number of sample analyses
- Commonly used to purchase supplies and less costly instruments or equipment
- The maximum size of a purchase order is set by the organization. In the federal government, purchase orders are limited to $100,000 (also called the "simplified acquisition threshold." A "micropurchase order" is authorized under FAR for purchases below $2,500. No justification or competition is required. Purchase orders between $2,501 and $100,000 are automatically set aside for "small businesses" unless justification can be made.

Noncompetitive procurement:
- Unusual or compelling urgency; Unique capabilities (such as a patent holder); National emergency
- Federal Acquisition Regulations specify procedures and justifications for limited competition at 6.302. A lack of funding or inadequate advance planning are insufficient justifications. ·

Invitation for Bid (IFB)
- Solicitation for proposals/offers issued under "sealed bid" procedures.
- Uncommon for laboratory services.
- A competitive bid process based solely on cost. Resulting contract is fixed-price.

Request for Quotation (RFQ)
- Solicitation for a task order under an existing federal supply schedule; all costs, terms, and conditions are already established
- May not change established terms and conditions, or exceed or enhance established scope and size
- A competitive bid process based mainly on cost, but may be on "best value"
- RFQ usually results in a fixed-price contract; best suited where requirements are readily defined in advance

5

- Request for Proposal (RFP)
- Basic Ordering Agreement (BOA) Doe uses - set of specs
- Modification (to Existing Contract)

Request for Proposal (RFP)
- Solicitation for proposals to establish contracts under FAR's negotiated procurement process
- Suitable for procurements where approach must be flexible or tailored to circumstances that can't be defined in advance
- Generally addresses a major long-term need for contractor support (several years)
- A competitive bid process based mainly on technical capability ("best value") rather than on price alone

Basic Ordering Agreement (BOA)
- Agreements established with one or more qualified laboratories to process samples
- BOA defines the analytes, costs, methods, APSs, MQOs, and any other parameters required
- Agency can send samples to one or several vendors depending on analyte, matrix, sample turnaround time, or the laboratory's ability to handle throughput
- Fixed-price or time-and-materials task orders
- Competitive procurement used to establish qualifications, capabilities, costs, capacities, and other requirements
- BOAs may be established with vendors under the Federal Supply Schedule (GSA) or by individual agencies. BOAs permit faster ordering because many of the prices, terms, and conditions are already established.
- BOAs establish the terms and conditions for indefinite delivery requirements (unknown quantities of task orders or analyses; unknown delivery dates for analyses or task orders; or both)

Modification to an Existing Contract
- Formal change to terms and conditions of a contract implementing options already built into the contract
- May be unilaterally imposed by government or bilaterally agreed upon
- Approach meets a need that is consistent with the type of contract that is in place
- Agency expands or extends contract to cover additional authorized work
- Agency amends contract to add a method for sample processing that is similar to work already covered
- Modifications must be authorized within the contract. For example, a contract with Acme Consultants to evaluate SOPs for tritium may not be modified to purchase tritium analyses without justifying sole source. Scope or quantity cannot be changed by a modification. But...
- If the original contract was for 100 tritium analyses, *and* contained a provision that the government could optionally order 100 strontium analyses, a modification may exercise that option.
- The government always reserves the right to modify contract unilaterally. If the modifications change the price, the contractor may seek "fair and equitable adjustments" in price.
- Many modifications are purely administrative and implement changes to terms and conditions. The name of the technical contact, for example.

6

- MARLAP recommends preparing written technical specifications ("statement of work"), regardless of whether the services are to be contracted out or performed by an organization's laboratory
- The SOW should contain the **Analytical Protocol Specifications** with MQOs
- Single most important parameter for SOW is the *required method uncertainty* at a specified concentration

- An MQO is a quantitative or qualitative statement of a performance objective or requirement for a particular method performance characteristic
- MARLAP recommends that an MQO for method uncertainty (u_{MR}) be established for each radionuclide/matrix combination
- The development of APSs, which includes the measurement quality objectives (MQOs), is described in detail in Chapter 3.
- The incorporation of these protocols into the relevant project plan documents is covered in Chapter 4.
- APSs should include such items as the MQOs, the type and frequency of quality control (QC) samples, the level of performance demonstration needed, number and type of samples, turnaround times, and type of data package.
- Other MQOs may include minimum detection capability, range, specificity, and ruggedness.

- Project plan documents
  - Obtain technical requirements needed to develop a SOW
  - MQOs and unique analytical process requirements contained in the APSs
- Level of specificity in the APSs limited to requirements that are **essential** to project's analytical data requirements

- Laboratory specifications to demonstrate ability to meet the technical specifications in the RFP
  - Method validation* and documentation requirements
  - Information from previous contracts for similar analytical work
  - Performance evaluation* programs
  - Sample delivery requirements
  - Quality system requirements

  past performance
  Re ...

  * See notes

- See example APS in handouts (Tab 14). The example APS has outlined the level of method validation required for a hypothetical project involving ^{90}Sr in milk. The level of method validation required depends on whether a laboratory has an existing ^{90}Sr method for milk or whether a method must be modified or developed for the milk matrix.
- PE programs may include:
  - Environmental Resources Associates (ERA) for EPA drinking water requirements
  - Department of Energy's Mixed Analyte Performance Evaluation Program (MAPEP) for environmental samples
  - Department of Energy's Quality Assurance Program (QAP)
  - ... various commercial vendors.

- **Inclusion of Analytical Protocol Specifications**
  - Analytes (5.3.1)
    - State radionuclides of interest, including expected concentration range when available
    - List possible interfering chemical and radionuclides, including expected concentration range when available
    - **MARLAP example: ^{90}Sr plus possible ^{89}Sr/fission products; interference from Ca, Ba, fat molecules**
  - Matrix (5.3.2)
    - **Descriptive not general form of matrix (e.g., solids); for MARLAP example, raw milk (fat content to vary)**

Review APS handout (Tab 14)

Analytes: Analyte list is complied from information obtained from process history and/or investigative studies.

Matrix: Matrix description should be provided for each radionuclide. A general description of matrix and (if possible) the chemical and physical properties of the matrix.

- Inclusion of Analytical Protocol Specifications
  - MQOs (5.3.3)
    - Detection or quantification; analyte concentration range; method specificity; method ruggedness
    - Required method uncertainty at a concentration (Action Level)
      "... method uncertainty = 0.5 pCi/L at 8 pCi/L ..."
    - Specificity (isolate and detect only the analyte of interest)
      "... ^{90}Sr plus possible ^{89}Sr/fission products interference..."
    - Ruggedness (matrix variations, change in analyst, slight changes in method steps while maintaining quality and performance)
      " ... raw milk (fat content to vary) ..."

Review APS handout (Tab 14).

- **MQOs:** MQOs may include required method uncertainty at the action level, the MDC (including Critical Level) or MQC, and the analyte concentration range, method specificity, and ruggedness. Method specificity is defined as "The ability of the method to measure the analyte of concern in the presence of interferences." Method ruggedness is defined as "The relative stability of method performance for small variations in method parameter values."

- **Unique analytical process requirements:** Unique analytical process requirements may be stated for sample preparation, chemical processing, or radiation/atom detection.

- **Action level** concentration may be incorporated in required method uncertainty statement.

- **Method Specificity** means the method's ability to isolate and detect only the analyte of interest.

- **Method Ruggedness** is the method's ability to handle matrix variations, change in analyst or slight changes in method steps while maintaining quality/performance specifications

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Interpret sji7

- Unique analytical process requirements (5.3.4)
- Other critical technical and quality specifications:
  - QC samples and PE Program requirements (5.3.5)
    - Schedule of batch QC and PE program
    - Criteria for acceptable performance
  - Radiological holding and TAT (5.3.6)   to report
    - Nuclide-specific; reporting of data
  - # Samples expected and schedule (5.3.7)
  - Quality System requirements (5.3.8)
  - Method selection and approval process (5.3.9)

8. Obtaining Laboratory Services   12

QC samples and PE Program requirements: Specifications on the type of batch QC samples and schedule of use (one set per batch of samples) should be provided. Also, the requirement to successfully participate in an external government or commercial performance evaluation program for the analytes and matrices of interest should be stated. Criteria for acceptable performance for batch QCs and successful participation in PE programs should be based on the MQOs.

Radiological holding and Turnaround Time (TAT): Specifications for radiological holding time will be related to the half-life of the radionuclide, radioanalytical method used, detection capabilities, and interfering nuclides and decay products. Turnaround time specifications will vary according project needs for the receipt of the analytical data. *TAT specifications can never be shorter than the radiological holding time*. TAT typically stated in routine, expedited, and emergency sample-processing time frames.

 # Samples expected and schedule: The SOW should state the estimated sample load, by schedule if possible. This information is important to evaluate the radioanalytical method proposed and the allocation of staff and equipment resources. Also, a commercial laboratory must ensure sufficient sample processing capacity for multiple clients sending samples at the same time.

Quality System requirements: If the organization or project requires the lab to use a certain Quality System process, details should be included in the SOW.

Method selection and approval process: The method selection and approval process should be stated in the SOW. This includes the method validation requirements (Chapter 6) for each combination of radionuclide and matrix and the acceptable criteria. Documentation requirements for method selection and validation should be included. Also, the TEC's evaluation process for method selection and validation should be included.

- Includes **Statement of Work**
- **Additional specifications** not included in the SOW
    - Quality, administrative, statutory, and regulatory requirements
    - Proposal instructions (technical and cost/business)
- RFP specifications usually included in resulting contract

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- Sample management plan (5.4.1)
- Licenses, permits, and environmental regulations (5.4.2)
- Laboratory accreditation (5.5.1)

5.4.1 Sample Management: The RFP should require the laboratory to have an appropriate sample management program that includes those administrative and quality assurance aspects covering sample receipt, control, storage, and disposition.

5.4.2 Licenses, Permits, and Environmental Regulations: Various federal, state, and local permits, licenses, and certificates (accreditation) may be necessary for the operation of a radioanalytical laboratory. The RFP should require the laboratory to have the necessary government permits, licenses, and certificates in place before the commencement of any laboratory work for an awarded contract. All federal contracts contain "boiler-plate" requirements for compliance with statutory mandates, such as recycling, insurance, liability, etc.

5.5.1 Accreditation: If accreditation is required in the RFP, the TEC should confirm the laboratory's accreditation for radioanalytical services. NELAC establishes and promotes performance standards for the inspection and operation of environmental laboratories in support of the National Environmental Laboratory Program (NELAP). If state-accredited, a laboratory typically is accredited by the state in which it resides, and if the state is a NELAP-recognized accrediting authority, the accreditation is recognized by other states and federal agencies approved under NELAP.

- Data reporting and communications (5.4.3)
- Sample re-analysis requirements (5.4.4)
- Subcontracted analyses (5.4.5)

5.4.3 Data Reporting and Communications: The type of information, schedules, and data reports required of the laboratory, as well as the expected communications between the appropriate staff or organizations, should be specified in the RFP. The SOW should specify what data are required for data verification, validation, and quality assessment.

- 5.4.3.1 Data Deliverables: A data package (sequentially page-numbered) may include a project narrative (in a specified format including units), a data review checklist, any non-conformance memos resulting from the work, sample-receipt acknowledgment or chain of custody form (if required), sample and quality control sample data, calibration verification data, and standard and tracer information.
- 5.4.3.2 Software Verification and Control
- 5.4.3.3 Problem Notification and Communication
- 5.4.3.4 Status Reports

5.4.4 Sample Re-Analysis Requirements: Specific instructions and contractual language should be included in the RFP that address such circumstances and the resultant fiscal responsibilities (Appendix E).

5.4.5 Subcontracted Analyses: MARLAP recommends that the RFP state that subcontracting of analyses will be permitted only with the contracting organization's approval. In addition, contract language should be included giving the contracting organization the authority to approve proposed subcontract laboratories.

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Laboratory Selection and Qualification Criteria

Technical Proposal Evaluation (5.5)

- Do not consider cost in technical evaluation process
- Scoring and evaluation scheme established prior to RFP distribution
  - Distributed to all prospective laboratories
- Technical Evaluation Committee
  - Each member evaluates the prospective laboratory's technical proposal
  - May not deviate from established scoring scheme

Continued...

5. Obtaining Laboratory Services 16

- Also refer to Appendix E, Section E.5. Proposal Evaluation and Scoring Procedures.

- Agency personnel initially involved in establishing a new contract and initiating the laboratory selection process may consists of: Contracting Officer (administrative, non-technical), Contracting Officer's Representative (technical staff person advising the Contracting Officer).

- Technical Evaluation Committee (TEC), a team of technical staff members, reviews the proposals sent by the laboratories. A chairperson is designated to provide oversight of the evaluation process. The TEC score the technical portion of each proposal according to the evaluation scheme established.

Technical Proposal Evaluation (5.5)

(...Continued)

- Scoring and evaluation scheme
  - Scoring elements
    - Technical merit
    - Adequacy and suitability of lab resources and equipment
    - Staff qualifications
    - Related experience and record of past performance
    - Other RFP requirements
  - Weighting of evaluation elements
    - Established before the RFP is distributed
    - If no weighting established, all are equal

Continued...

- **5.5.1.1 Scoring and Evaluation Scheme:** The RFP should include information concerning scoring of proposals or weighting factors for areas of evaluation. This helps a laboratory to understand the relative importance of specific sections in a proposal and how a proposal will be evaluated or scored.

- **5.5.1.2 Scoring Elements**

   Technical Merit: *The lab's proposal (in response to RFP) should include details of the laboratory's quality system and all the analytical methods to be employed by the laboratory as well as the method validation documentation. The methods should be evaluated against the APSs and MQOs provided in the SOW. Previous performance should be reviewed and scored.*

   Adequacy and Suitability of Laboratory Resources and Equipment: If requested in the RFP, the laboratory will provide a listing of the available instrumentation or equipment by analytical method category. In addition, the RFP may have requested information on the available sample processing capacity and the workload for other clients during the proposed contract period.

   Staff Qualifications: The RFP should require the identification of the technical staff and their duties, along with their educational background and experience in radiochemistry, radiometrology, or laboratory operations. The laboratory staff that will perform the radiochemical analyses should be employed and trained prior to the award of the contract.

   Related Experience and Record of Past Performance: The RFP should require the laboratory to furnish references in relation to its past or present work.

   Other RFP Requirements: The laboratory's proposal should outline the various programs and commitments (QA, safety, waste management, etc.) as well as documentation of various certifications, licenses, and permits to ensure the requirements of the RFP will be met.

   Also refer to Appendix E, Section E.5. Proposal Evaluation and Scoring Procedures.

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Technical Proposal Evaluation (5.5)

(...Continued)

Technical Merit —

- Review of lab's proposed methods to satisfy APS/MQOs for each nuclide/matrix combination
- Review of the method validation documentation to determine if method uncertainty specifications are met
- Review of past performance in PE programs and internal QA program

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Section E5.3: Weighting of evaluation elements (example)

Element	Description	Weight (%)
I	Technical Merit	25
II	Past Performance	25
III	Understanding of the Requirements	15
IV	Adequacy and Suitability of Proposed Equipment and Resources	15
V	Academic Qualifications and Experience of Personnel	10
VI	Related Experience	10

5.5.1.2 Scoring Elements Technical Merit: The lab's proposal (in response to RFP) should include details of the laboratory's quality system and all the analytical methods to be employed by the laboratory as well as the method validation documentation. The methods should be evaluated against the APSs and MQOs provided in the SOW. Previous performance should be reviewed and scored.

Adequacy and Suitability of Laboratory Resources and Equipment: If requested in the RFP, the laboratory will provide a listing of the available instrumentation or equipment by analytical method category. In addition, the RFP may have requested information on the available sample processing capacity and the workload for other clients during the proposed contract period.

Staff Qualifications: The RFP should require the identification of the technical staff and their duties, along with their educational background and experience in radiochemistry, radiometrology, or laboratory operations. The laboratory staff that will perform the radiochemical analyses should be employed and trained prior to the award of the contract.

Related Experience and Record of Past Performance: The RFP should require the laboratory to furnish references in relation to its past or present work.

Other RFP Requirements: The laboratory's proposal should outline the various programs and commitments (QA, safety, waste management, etc.) as well as documentation of various certifications, licenses, and permits to ensure the requirements of the RFP will be met.

• **Weighting of each element (See Section E5.3 in Appendix E)**

Example weighting. Anticipated weights should be listed in RFP. (If divulged in RFP, weights may not be changed without notifying proposers.)

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- Pre-award proficiency evaluation (5.5.2)
  - PT samples sent to most qualified labs to assess each lab's capability to meet MQOs and RFQ requirements
  - Scoring of each lab's performance
  - Ranking or weighting of each lab's performance as a separate scoring element

- Pre-award assessments and audits (5.5.3)
  - Emphasizes availability of instruments, facilities, staff, quality system manual, methods, calibrations, etc.
  - Potential to handle the anticipated volume of work

5.5.2 Pre-Award Proficiency Evaluation: Some organizations may elect to send proficiency or PT samples (sometimes referred to as "performance evaluation" or "PE" samples) to the laboratories that meet a certain scoring criterion in order to demonstrate the laboratory's analytical capability. The composition and number of samples should be determined by the nature of the proposed project.

5.5.3 Pre-Award Assessments and Audits: The RFP should indicate that the laboratories with the highest combined scores for technical proposals and proficiency samples may be given an on-site audit. A pre-award assessment or audit may be performed to provide assurance that a selected laboratory is capable of fulfilling the contract in accordance with the RFP.

MARLAP Recommends...

- Technical specifications contained in a single document ("SOW") for all radioanalytical laboratory services, regardless of whether the services are to be contracted out or performed by an affiliated laboratory
- MQOs and analytical process requirements contained in the SOW are provided to the laboratory
- SOW includes the specifications for the action level and the required method uncertainty for the analyte concentration at the action level for each analyte/matrix combination

Continued...

- Laboratory submits proposed methods and required method validation documentation with the formal response

- RFP permits subcontracting only with the contracting organization's approval

- All members of the TEC have a technical understanding of the subject matter related to the proposed work

Method Validation:
Performance-Based Approach

Module 9

Dave McCurdy

- Part I
  - Concepts and information prepared for **Project Managers**

- Chapter 6 is <u>**different**</u> than rest of Part I
  - Concepts and information prepared for
    - Radioanalytical Specialists, Technical Evaluation Committee, Project Managers
    - Laboratory managers and staff

  - Both audiences need to understand the material to successfully implement
    - Performance-based method selection
    - Method validation

2

Method Definition (6.2)

A laboratory "method" includes all physical, chemical, and radiometric processes conducted at a laboratory in order to provide an analytical result

MARLAP Analytical Process

Field Sample Preparation and Preservation → Sample Receipt and Tracking → Laboratory Sample Preparation → Sample Dissolution → Chemical Separation → Sample Preparation for Instrument Measurement → Instrument Measurement of Radionuclides → Analytical Calculations and Data Reduction → Data Verification, Validation and Reporting

May be Included

These Steps Are Typically Considered to be "The Method"
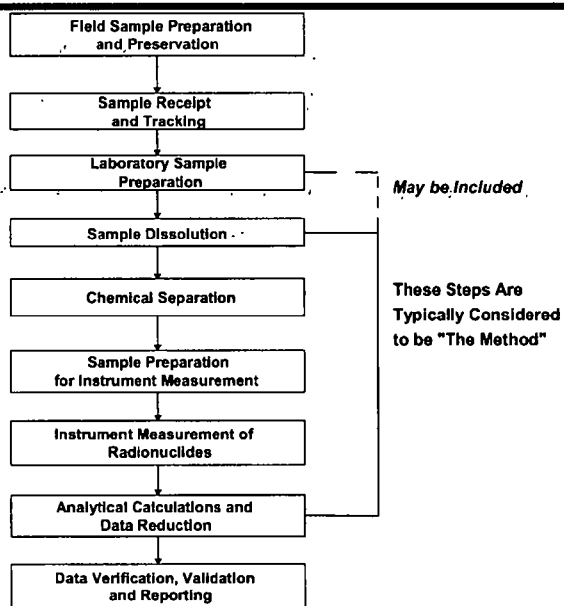
Process to select a validated method based on a demonstrated capability to meet defined quality and performance criteria (MQOs) and (together with a properly implemented QA program) will produce appropriate and technically defensible results under the applicable conditions

Objective: To facilitate the evaluation of all relevant and applicable methods with the selection, modification, or development of the method that will reliably produce the data as defined by the criteria of the directed planning process (measurement quality objectives).

Intent: To allow the selection of the method that meets the MQOs to the discretion of the laboratory performing the work or, in some cases, to the discretion of a client organization. In most project plan documents, the project manager has the authority and responsibility for approving and/or selecting the methods proposed by the laboratory.

Prescribed-Method Approach

- Option of specifying a particular method in:
  - quality assurance project plan
  - statement of work
- Recognized "prescribed methods".
- In most cases, these methods have undergone some type of validation process for their intended use

Recognized "prescribed" methods include:

- Regulatory – e.g., EPA

- National industry standards {International Organization for Standardization (ISO), American Society for Testing and Materials (ASTM), American National Standards Institute (ANSI), Official Methods of Analysis of AOAC International - Association of Official Analytical Chemists International, Standard Methods for the Examination of Water and Wastewater

- Industry-specific (historically developed for internal use within a specific organization/company).

6

- MARLAP Key Parameters – MQOs
  - Most important parameter is required method uncertainty (u_{MR}) at a specified concentration

Performance-based approach to method selection (6.3):

- Laboratory selects and proposes a method(s)
- Project Manager (or TEC) approves use of proposed method

Project Manager (or technical evaluation committee) approves use of proposed method: Evaluates submitted method validation documentation or evaluates performance of lab's analysis of method-validation PT samples.

Upon contract award: APSs/MQOs should be incorporated into a specific project work plan for the laboratory.

Project-Specific Considerations for Method Selection (6.5)

- Matrix and analyte (radionuclide) identification (6.5.1)
- Process knowledge (6.5.2)
  - Potential chemical and radionuclide interferences
- Radiological holding and turnaround times (6.5.3)
- Unique process specifications (6.5.4)
- MQOs (6.5.5)
- Bias considerations (6.5.5)
- Operational aspects

9. Method Validation   9

MQOs may include:

- Method uncertainty [u_{MR}] at the action level
- Quantification capability (MQC) or minimum detection capability (MDC)
- Expected/applicable analyte concentration range
- Method specificity
- Ruggedness

Operational aspects may include:

- Available methods validated for analyte/matrix combinations
- Qualified staff availability
- Equipment calibration and availability
- Production schedule and proposed number of samples

- Laboratory must consider:
  - APSs & MQOs
  - Methods available for nuclide/matrix
  - Method validation status
  - Availability of qualified staff   /capacity
  - Production schedule & number of samples
  - Radiological holding and sample turnaround times
  - Equipment calibration and availability, etc.   \capacity

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Project Manager:

- Reviews documentation and PE program performance
- Evaluates response to other performance/ production requirements
- If possible, compares submitted methods to other existing or known methods
- Evaluates response to other performance/ production requirements

Continued...

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Project Manager (Continued):

- Makes decision to send pre-award, site-specific performance testing matrix samples

- Makes decision to perform pre-award, onsite laboratory, or desk audit

- From additional information, makes list of capable laboratories (technical basis only)

- Laboratory selection (Contracting Officer)

MARLAP provides guidance only on project-specific method validation, not general method validation.
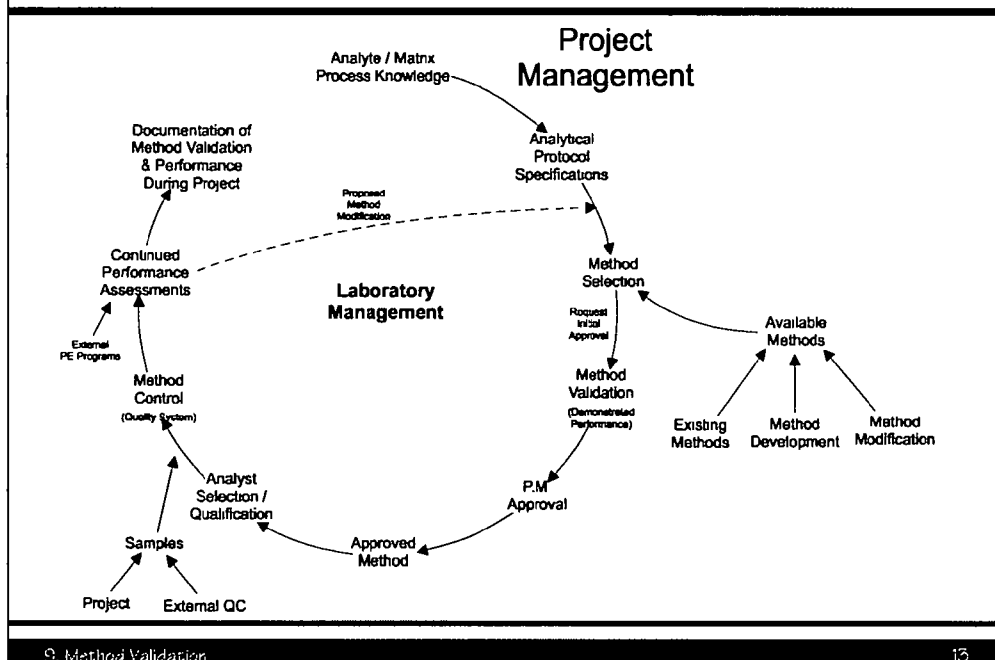
Project Method Validation

- Process demonstrating that the radioanalytical method selected for the analysis of a particular radionuclide in a given matrix is capable of providing analytical results to meet the project's measurement quality objectives and any other requirements in the analytical protocol specifications

General Method Validation

- The laboratory's internal method validation process that demonstrates a method's performance to meet established* quality performance requirements for detection and quantification, especially precision and bias requirements

* Not specific to project

Two types of method validation are considered in Section 6.6:

- General

- Project-specific

MARLAP provides guidance on project-specific method validation, not general method validation

General method validation process (Section 6.6.1): Should be a basic element in a laboratory's quality system. General guidance on single laboratory method validation can be found in IUPAC (2002) and EURACHEM (1998). For most applications, the method should be evaluated for precision and relative bias for several analyte concentration levels. In addition, the absolute bias, critical level and the *a priori* minimum detectable concentration of the method, as determined from appropriate blanks, should be estimated. (See Section 6.6.4 for a discussion on testing for absolute and relative bias.)

EURACHEM. 1998. *The Fitness for Purpose of Analytical Methods, A Laboratory Guide to Method Validation and Related Topics*. ISBN 0-948926-12-0. Available at: www.eurachem.ul.pt/index.htm.

International Union of Pure and Applied Chemistry (IUPAC). 2002. "Harmonized Guidelines for Single-Laboratory Validation of Methods of Analysis." *Pure Appl. Chem.*, 74:5, pp. 835-855.

Project Method Validation

Laboratory Initiation*

- Accomplished by the laboratory by processing internal, external PT, or Method Validation Reference Material (MVRM) samples according to the validation level specified by the Project Manager or Technical Evaluation Committee (TEC)

Project Manager Initiation (Optional)**

- Accomplished by the Project Manager sending PT samples to the laboratory

Review notes

9. Method Validation   15

* Chapter 6 provides details for this approach.

** Not specifically covered in Chapter 6. However, the same approach would be used by the project manager.

Prior to submitting PT sample to laboratory, the method validation level must be selected, and the radioanalytical results of the PT samples evaluated according to the method validation acceptance criteria.

Parameters specified or ascertained (including interferents) from the analytical results generated from DQOs & process history research:

- APSs including MQOs for each analyte/matrix
- Defined method validation level (Slide 19)
- Analytes and testing range
- Defined matrix for testing, including chemical and physical characteristics that approximate project samples or...

Continued...

APSs including MQOs for each analyte/matrix (see handout): Plus bias restrictions (if applicable) and other qualitative parameters to measure the degree of method ruggedness or specificity.

Analytes: Chemical or physical characteristics of analyte when appropriate.

Applicable analyte concentration range: Includes zero analyte (blanks).

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Project Method Validation Protocol Parameters
(Continued)

- Selected project-specific or appropriate alternative matrix PT samples, including known chemical or radionuclide interferences at appropriate levels
- Defined sample preservation
- Stated additional data testing criteria
- Establish acceptable chemical/radiotracer yield values
- Bias (if applicable)

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- Level of method validation necessary is established during project planning – Project Manager responsible to ensure level of method validation is included in SOW
- Level of validation depends on the degree of confidence in the method's performance to produce results consistent with the required method uncertainty
- Level of validation depends on the extent of method development, specificity, and ruggedness

9. Method Validation   18

Level of validation depends on the extent of method development, specificity and ruggedness:

- New radionuclide or set of interferences
- Matrices consistent with previous applications
- Radionuclide concentration range consistent with other projects
- Modification of existing method

Validation Level	Application	Sample Type*	Acceptance Criteria§	Levels† (Concen.)	Replicates
A (Without Additional Validation)	Existing Validated Method	—	Method Previously Validated (By One of the Validation Levels B through E)	—	—
B	Same or Similar Matrix	Internal PT	Measured Value Within $\pm 2.8 u_{MR}$ or $\pm 2.8 \varphi_{MR}$ of Known Value	3	3
C	Similar Matrix/New Application	Internal or External PT	Measured Value Within $\pm 2.9 u_{MR}$ or $\pm 2.9 \varphi_{MR}$ of Known Value	3	5
D	Newly Developed or Adapted Method	Internal or External PT	Measured Value Within $\pm 3.0 u_{MR}$ or $\pm 3.0 \varphi_{MR}$ of Known Value	3	7
E	Newly Developed or Adapted Method	MVRM Samples	Measured Value Within $\pm 3.0 u_{MR}$ or $\pm 3.0 \varphi_{MR}$ of Known Value	3	7

See handouts for footnotes and following slide.

* PT and MVRM samples should be traceable to a national standards body, such as NIST in the United States. Internal PT samples are prepared by the laboratory. External PT samples may be obtained from a performance evaluation program or from a commercial radioactive source producer that has traceability to a national standards body. Blank samples should be representative of the matrix type being validated.

§ The acceptance criterion is applied to each analysis in the method validation, not to the mean of the analyses. u_{MR} is the required absolute method uncertainty for analyte concentrations at or below the action level and φ_{MR} is the required relative method uncertainty for analyte concentrations above the action level (see Figure C.1 in Appendix C). The acceptance criteria are chosen to give a false rejection rate of ~5% when the measurement process is unbiased, with a standard deviation equal to the required method uncertainty (u_{MR} or φ_{MR}).

† Concentration levels should cover the expected analyte concentration range for a project including the action level concentration. A set of five appropriate blanks (not considered a level) should be analyzed during the method validation process. The blank data and the estimated absolute bias in the mean blank concentration value (see Attachment 6A in this chapter for applicable statistical tests) shall be reported as part of the method validation documentation.

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Important Notes for Table

- *Acceptance Criterion*
  - Established so that every validation sample must meet the stated limit
  - Varies according to the number of validation samples (degrees of freedom) to be consistent with a false rejection rate of 5% when the measurement process is unbiased
  - Incorporates the required method uncertainty at the action level

- *Concentration Range*
  - Should cover the expected analyte concentration range including the action level concentration
  - 5 appropriate blanks included (but not as a test level) to estimate the absolute bias of the method

- Existing Methods Requiring No Additional Validation (6.6.3.1)
- Use of a Validated Method for Similar Matrices (6.6.3.2)
- New Application of a Validated Method (6.6.3.3)
- Newly Developed or Adapted Methods (6.6.3.4)

- **Level A Validation**
  - Method previously has been validated (Levels B – E)
  - Matrix and analytes of new project sufficiently similar to past samples analyzed by a lab's SOP
  - Project Manager assumes additional validation is unwarranted

Caution

Without some degree of validation for a new project, there is no assurance that the lab will perform to the same quality and standards as an extension of earlier work

The MARLAP example for ^{90}Sr in milk requires a Method Validation Level of A, C, or D (as specified in the APS/SOW) depending on whether the laboratory has an existing method for ^{90}Sr in milk or whether a method must be modified or developed for ^{90}Sr in milk.

Level A Project Method Validation

1) **New Client Project: Evaluation of Drinking Water**
- Use EPA approved method
- Method validated previously under Level C (External PT)
- Previous and ongoing acceptable performance in EPA Performance Evaluation Program
- Method use: continuously

2) **New Client Project: Evaluation of ^{90}Sr in Raw Milk**
- Modified an EPA approved method for ^{90}Sr in water to be used for raw milk
- Method validated previously under Level C (Internal PT)
- Previous and ongoing acceptable performance in internal performance testing program and other client PE programs
- Method use: continually for other clients

Additional New Client Project Example: Radium-226 in soil by alpha spectrometry

- Expanded contract to include processing soil samples from new area in the same uranium mining and milling remediation site
- Method validated under Level C (Internal PT) samples for similar project for adjacent area during the previous year

Level B validation

- Lab has a routine method for a specific radionuclide/matrix combination that has had no previous project method validation

- Requires evaluating method with internal PT samples at 3 concentration levels, with 3 replicates per level

- Lab should have sufficient information on the performance of the method using its internal quality control (QC) program and external Performance Evaluation (PE) programs.

- Lab has a routine method for a specific radionuclide/matrix combination that has had no previous project method validation (e.g., the lab method was derived "in-house" or does not match the American Society for Testing and Materials (ASTM) or EPA method that may have been referenced in the SOW).

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Level B Project Method Validation – Same Matrix

New Client Project: Surveillance of ^{90}Sr in raw cow milk

- Laboratory has routine method under general validation but not used for five years
- Expected sample matrix similar to previous milk samples
- Records of past performance in a PE program or internal QA not available

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- Analysis of samples that are similar to the matrix and analyte for which a previously method was developed
  - Validation of the method according to Level B or C

- Validation levels will provide a reasonable assurance that the method will meet the required MQOs

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Level B validation requires evaluating method with internal PT samples at 3 concentration levels, with 3 replicates per level

- Requires that each result be within ±2.8 u_{MR} or ± 2.8 φ_{MR} of known value

Level C validation requires evaluating the method with internal or external PT samples at 3 concentration levels, with 5 replicates per level

- Each result within ±2.9 u_{MR} or ±2.9 φ_{MR} of known value
- For ^{90}Sr example: ±1.45 pCi/L or ±18% of known value

Example for ^{90}Sr in milk: Requires a method validation level of A, C, or D (as specified in the APS/SOW), depending on whether the laboratory has an existing method for ^{90}Sr in milk or whether a method must be modified or developed for ^{90}Sr in milk.

Level B validation: Requires the least amount of effort for the laboratory but may not satisfy the level of method validation required by the project.

- When the laboratory does not have the capability to produce internal QC samples, the Level C validation protocol should be used.

- Requires that each result be within ±2.8 u_{MR} or ± 2.8 φ_{MR} of known value depending on the test level concentration.

Level C validation: A change in the method to address the increased heterogeneity of the analyte distribution within a sample may require another method validation depending on the ruggedness of the method and the degree of analyte heterogeneity.

- Requires a greater effort for the laboratory compared to Level B validation.

- Level C validation requires that each result be within ±2.9 u_{MR} or ± 2.9 φ_{MR} of known value depending on the test level concentration.

- For the APS ^{90}Sr example, Level C Validation requires each result to be within ± 1.45 pCi/L of the known value below the action level or ± 18% of the known value at or above the action level.

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Level B or C Project Method Validation – Similar Matrix

New Client Project: Surveillance of ^{90}Sr in raw goat milk
- Laboratory has a validated method for ^{90}Sr in cow's milk that has been used routinely for the past eight years
- Expected sample matrix similar to cow's milk but analyte concentration expected to be higher than milk from cows in the same area
- Expected sample size is less but is only a concern for reprocessing a backup sample
- Use of client goat milk with spike is option for method validation (samples from a batch composite)
  - One portion of the composite used to make the spiked test samples.
  - Another portion of the composite used as blank samples to determine the inherent ^{90}Sr in the samples

For slight changes in matrices, Validation Level B is typically required.

Additional New Client Project Example: Analysis of ^{90}Sr in soil from new site
- Laboratory has a validated method for ^{90}Sr in soil from the northeast United States that has been used routinely for the past five years
- Expected sample matrix from different region will contain high levels of iron compared to the soils of the northeast
- To meet detection detection and quantification requirements, sample size for analysis must be the same as the northeast samples
- Existing method must be slightly modified to address the increased iron content
- *Project Manager requires Validation Level C*

New applications include:

- Dissimilar matrices
- Chemical speciation of the analyte or possible other chemical interference
- Analyte, chemical or radiometric interferences
- Complete solubilization of the analyte and sample matrix
- Degree of analyte or sample-matrix heterogeneity

Methods that have been validated for one application normally require another validation for a different application, such as a different sample matrix.

The validation process for an existing validated method should be reviewed to ensure applicability of the new (which can be more or less restrictive) MQOs because MQOs may change from one project to another or from one sample matrix to another.

Applying an existing method to another matrix is not recommended without further method validation.

Level C validation requires evaluating the method with internal or external PT samples at 3 concentration levels, with 5 replicates per level

- Each result within $\pm 2.9\ u_{MR}$ or $\pm 2.9\ \varphi_{MR}$ of known value
- For ^{90}Sr example: ± 1.45 pCi/L or $\pm 18\%$ of known value

For the APS ^{90}Sr example, Level C validation requires that each result must be within $\pm$ 1.45 pCi/L of the known value below the action level or $\pm$ 18% of the known value at or above the action level.

Level C Method Validation – New Application

New Client Project: Surveillance of ^{90}Sr in raw cow's milk
- Laboratory has a method for ^{90}Sr in drinking water that was modified to be similar to U.S. Public Health Service method for ^{90}Sr in milk by ion exchange
- New method has undergone general method validation
- Method has been used in the analysis of PT samples from a commercial PE program with success

Project Manager requests Method Validation Level C with external PT samples from a selected commercial source supplier

- Methods that have been validated for one application normally require another validation for a different application, such as a different sample matrix.
- The validation process for an existing validated method should be reviewed to ensure applicability of the new (which can be more or less restrictive) MQOs because MQOs may change from one project to another or from one sample matrix to another.

Additional examples:
- New Client Project: Analysis of ^{90}Sr in samples from low-level contamination of reactor components (drained water stored in composite tank sample)
    - Existing validated method for ^{90}Sr in drinking water that has been modified to include additional cleanup and purification steps for other interfering radionuclides in the sample
    - Expected sample matrix similar to water but is acidified and may have some detergent
    - Other radionuclide analyses are to be performed on the sample
    - ^{89}Sr will interfere
    - Method Validation Level C may be appropriate for this application
- New Client Project: Change in sample preparation for ^{239}Pu in Soil Analysis
    - Existing validated method for ^{239}Pu in soil that uses acid digestion/ leaching preparation for 10 g of dried, blended soil
    - New client requests total dissolution by pyrosulfate fusion of 5 g of dried, blended soil
    - Beginning of method must be modified to include the pyrosulfate fusion and then to handle the chemical interference from the fusion process
    - Project Manager requests Method Validation Level C with external PT samples prepared (spiked) by a commercial source supplier

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- Lab modified its ^{90}Sr method for water to be applicable for milk*
- Lab uses internal PT samples prepared from fresh milk:
  - 5 milk samples spiked with ^{90}Sr at 3 pCi/L; 5 spiked at 9 pCi/L;
  - 5 spiked at 25 pCi/L
  - For lowest spike level (3 pCi/L), each result must be within ±2.9 u_{MR} of known value:

    ± 2.9 × 0.5 pCi/L = ±1.45 pCi/L of known; between 1.55 and 4.45 pCi/L
  - For two highest spike levels, each result must be within ±2.9 φ_{MR} of known value:

    ±2.9 × 6.25% = ± 18% of known; for the mid level spike (9 pCi/L) this is ± 1.6 pCi/L of known or between 7.4 and 10.6 pCi/L; for the upper level spike (25 pCi/L) this is ±4.5 pCi/L of known or between 20.5 and 29.5 pCi/L

*Review notes

* Because the needed chemical purification steps are unique to a milk matrix, some may consider *Level D* validation more appropriate.

Newly Developed or Adapted Methods (6.6.3.5)

- New method developed by laboratory not previously validated by laboratory
- Use of a published method (literature or nationally recognized standard) not previously validated by laboratory
- Adaptation of a published method (literature or nationally recognized standard) not previously validated by laboratory
- For routine or common matrices, Method Validation Level D is required
- For special project matrices, Method Validation Level E using Method Validation Reference Material (MVRM) test samples is required
  - Project Manager supplies MVRM test samples

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**Newly Developed or Adapted Methods
(6.6.3.5)**

Level D validation: Internal or external PT samples at 3 concentration levels, with 7 replicates per level

- Requires that each result be within ±3.0 u_{MR} or ±3.0 φ_{MR} of known value
- For ^{90}Sr example: ±1.5 pCi/L or ±19% of known value

Level E validation: MVRM samples at 3 concentration levels, with 7 replicates per level

- Requires that each result be within ±3.0 u_{MR} or ±3.0 φ_{MR} of known value

When the matrix under consideration is unique, the method should be validated using the same matrix (e.g., MVRM) under Level E Validation. For example, process/effluent waters versus laboratory deionized water and for various heavy metal radionuclides in soils or sediments when compared to spiked sand or commercial topsoil. For site-specific materials containing severe chemical and radionuclides interferences (for example, sludge from a tank that has been dewatered), many methods have been unable to properly address the magnitude of interferences.

The MARLAP example for ^{90}Sr in milk requires a Method Validation Level of A, C, or D (as specified in the APS/SOW), depending on whether the laboratory has an existing method for ^{90}Sr in milk or whether a method must be modified or developed for ^{90}Sr in milk.

For the APS ^{90}Sr example, Level D validation requires that each result must be within ± 1.5 pCi/L of the known value below the action level or ± 19% of the known value at and above the action level.

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Level D Method Validation: Newly Developed Method

New Client Project: Analysis of ^{129}I in groundwater
- Senior radiochemist and radiation spectrometrist at laboratory develop new ^{129}I radiochemical method based on radiochemistry fundamentals and available nuclear instrumentation
  - Method formulation incorporated the sample size, sample preparation, chemical separations, final test sample mount and ^{129}I detection efficiency to meet APSs
  - No short-lived iodine isotopes expected
  - Low-energy photon detector used

Additional examples:

- New Client Project: ^{90}Sr in drinking water samples
  - Standard operating procedure was prepared that incorporated all steps of EPA Published Method 905.0 or EML Procedure Manual Method SR-02

- New Client Project: Thorium-230 and ^{232}Th in soil samples having unique characteristics
  - Soil samples from a contaminated U/Th site
  - APSs incorporate historical site knowledge of U and Th concentrations
  - New laboratory prepared SOP for Th in soil that incorporated all steps of a recognized method
    o Th-234 tracer to determine the chemical yield of each sample
    o Th-234 a decay product of ^{238}U
  - Project Manager requires Method Validation Level E and provides MVRM samples to determine if the proposed method will meet the necessary Th and U specificity requirements and the Th chemical yield determinations are not biased by the highest levels of U in the anticipated sample population

Method Bias Should be Evaluated...

- Initially — Method validation process
- Continuously — Quality assurance program via batch QC

Two types of bias

- Absolute:
  - Mean response at zero concentration

- Relative:
  - Ratio of the change in the mean response to a change in sample analyte concentration

intercept

slope

Absolute Bias: evaluates the mean response at zero concentration.
- Testing for absolute bias involves repeated analyses of method blank samples
- Method validation should include blank samples to assess absolute bias

Considerations:
- Absolute bias in the measurement process can lead to incorrect detection decisions. Causes include inadequate corrections made by the laboratory for instrument background, laboratory reagent contamination, and other interferences.
- The laboratory should eliminate any absolute bias in the measurement process by blank- or background-correcting all measured results.
- Test whether the corrections are adequate by analyzing a series of *method blank* samples, applying all appropriate corrections exactly as for ordinary samples, and perform a *t*-test on the results.
- To avoid the appearance of a false bias, the determinations of the correction terms (e.g., background or reagent blank) should be repeated for each method blank sample analyzed.

Relative Bias: Ratio of the change in the mean response to a change in sample analyte concentration.
- Testing for relative bias requires repeated testing of spiked samples
- Use either standard reference materials (SRMs) or certified reference materials (CFMs)
- Replicate samples at each testing concentration level

Considerations:
- Testing the method for relative bias is most important when one of the purposes of analysis is to determine whether the analyte concentration is above or below some positive action level.
- To test for relative bias, the laboratory may analyze an appropriate Certified Reference Material (or spiked sample) a number of time.
- To avoid the appearance of a false bias, the laboratory should replicate as many steps in the measurement process as possible for each analysis.

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Depending on Project...

- Absolute bias at a certain analyte concentration may be the most important consideration
  - Action Level
    - May want no statistical or major bias at the action level: premise of required method validation application

  - Blank Samples
    - For certain research or survey projects, no absolute bias near the the detection limit

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Bias test when analyte concentration ≠ 0.0

$$|T| = \frac{|X_{avg} - K|}{\sqrt{s^2/N + u^2(K)}}$$

X_{avg} = average measured value
s   = experimental standard deviation
N = number of measurements
K = reference value
u(K) = standard uncertainty for reference value
T   = experimental T-statistic

Bias when |T| > t $_{1-\alpha/2}$ @ (v_{eff})

t $_{1-\alpha/2}$ = t statistic with significance level α (typical 0.05)
v_{eff} = degrees of freedom

The number of *effective degrees of freedom* (v_{eff}) is calculated as follows:

$$v_{eff} = (N - 1) \times (1 + (u^2[K] / [s_x^2 / N]))^2$$

Absolute bias test when analyte concentration = 0.0

$$|T| = \frac{|X_{avg}|}{\sqrt{s^2/N}}$$

X_{avg} = average measured value

s = experimental standard deviation

N = number of measurements

- Analyte concentration = 0.0
- Data from 9 batch QC samples

0.714	0.993
2.453	0.472
-1.159	-0.994
0.845	0.673
0.495	

X_{avg} = 0.4991
s = 1.0745

$$|T| = \frac{|X_{avg}|}{\sqrt{s^2/N}}$$

$$|T| = \frac{0.4991}{\sqrt{(1.0745 \times 1.0745)/9}} = \frac{0.4991}{0.3582} = 1.3935$$

$v_{eff} = 9 - 1 = 8$

$t_{1-\alpha/2} @ (v_{eff}) = 2.306$ (Table G.2 in Appendix G)

T < t: 1.3935 < 2.306

... No bias is detected

Option 1: Weighted Least Squares (6A.3)

- Perform a weighted linear regression to fit a straight line to the data and perform hypothesis tests to determine whether the intercept = 0 and the slope = 1

Weighted Least Squares (6A.3): Weighted linear regression fit to the data and perform hypothesis tests to determine whether the slope = 1

- 5 blank sample measurements
    - Separate test level if known analyte concentration = 0
    - Mean value to be subtracted from each test result
- Requires multiple measurements at three analyte test levels
    - Number of test samples/level either 3, 5, or 7

Option 2: Overall Method Bias (6A.3)

- Evaluate overall method bias for all test levels
- An overall α' is used instead of the significance level α (typical 0.05)
- Evaluate each test level for bias using the overall α' value

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- Test for overall method bias for all concentration levels
- Requires testing each concentration level but use a "t" value based on a value α' instead of α:

$$t_{1-\alpha/2} @ (\nu_{eff}) \text{ or } t_{1-\alpha'/2} @ (\nu_{eff})$$

$$\alpha' = 1 - (1-\alpha)^{1/m}$$

m = number of test levels
If $\alpha = 0.05$ and m = 3, then $\alpha' = 0.01695$

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Testing for Method Bias (6A.3)
Bias Tests for Multiple Test Levels

- Test for overall method bias for all concentration levels
- If all bias tests using the α' value for every test level indicates no bias, then
  - method considered free of bias based on an α false rejection rate over the concentration range evaluated

9. Method Validation   45

Note: For method validation, there would be 5 blank test samples, three test levels and depending on the validation level either 3, 5, or 7 test samples per test level

When laboratory conducts method validation

- All records, laboratory workbooks, and matrix spike data used to validate an analytical method should be retained on file

When Project Manager conducts method validation (PT samples sent to laboratory)

- Appropriate technical representative should retain all records dealing with applicable method validation protocols, PT sample preparation certification, level of validation, results, and evaluations

Laboratory conducts Method Validation – Covered in Section 6.6.5:

- The records and MV documentation should be retrievable for a specified length of time after the method has been discontinued (reports to the Project Manager containing these method validation data should be retained in the project records or QAPP).
- Data evaluations such as comparison of individual results to the validation acceptance criterion and absolute bias in blanks and, when available, method precision and bias, should be part of the data validation package sent to the project manager.
- All method validation documentation should be retained as part of the documentation related to the laboratory's quality system.

Project Manager Validates Method (PT Samples to Lab) – Expected documentation:

- Evaluations include comparison of individual results to the validation acceptance criterion, absolute bias in blanks and, if available, statistical analyses of the data for method precision and bias.
- Laboratory should provide the necessary documentation to the project manager for these PT samples as required by the SOW.
- Laboratory should request feedback from the project manager as to the method performance.
- Information, along with the sample analytical results documentation, should be retained by the laboratory for future method validation documentation.

Method Selection Life Cycle Documentation (6.10)

Information gathered during the use of the method

- Method validation protocol and results
- Analyst training and proficiency tests
- Method manual control program
- Instrument calibration and QC results
- Internal QC and external PT sample result
- Internal and external assessments
- Corrective actions

Should be part of the quality system documentation

MARLAP Recommends...

- Performance-based approach for method selection
- Only methods validated for a project's application are used
- SOW containing the MQOs and analytical process requirements provided to the laboratory
- SOW includes specifications for the action level and required method uncertainty (u_{MR}) for the analyte concentration at the action level for each combination of analyte and matrix

Continued...

MARLAP Recommends...
(Continued)

- Method undergoes some basic general validation prior to project method validation

- Method applied to a specific project should undergo validation for that specific application

- As each new project is implemented, the methods used in the analysis of the samples undergo some level of validation (*Project Manager's responsibility to assess the level of method validation necessary*)

- Tiered approach for project method validation

Method Validation Discussion Period

- Does the audience have questions about the validation levels for methods used in their projects?
- Take 15 minutes to:
  - Develop a method validation plan
  - Evaluate an example validation data set for validation requirements based on required method uncertainty

Evaluating Methods and Laboratories

Module 10

Dave McCurdy

and

Bob Litman

Overview

This section of MARLAP examines:

- Proposed method evaluation
- Laboratory selection

Needs to satisfy:

- Measurement Quality Objectives (MQOs)
- Method validation requirements
- Regulatory requirements
- Data deadlines
- Project costs

The selected method must:

- Be able to achieve the MQOs for the analyte
- Be specific for the analyte or analytes
- Be suitable for the matrix
- Be applicable to the amount of sample that will be available
- Be able to be performed in a timely manner
- Have a reasonable cost based on project requirements

Proposed method should not be based on:

- Previously identified methods for the same analyses
- Capricious request for the "best" method
- The only method that a particular laboratory has for the analysis

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	Soil	Milk	Water	Grass
^{90}Sr		★		
^{137}Cs				
^{14}C				
^{3}H				

We are focused in this example on strontium in milk. But if we had a project with the indicated matrices and analytes, we may need to assess a method for each of combinations.

- Technical evaluation committee (TEC) or radioanalytical specialist considers whether proposed method is appropriate based on project requirements
- What considerations affect method evaluation?
  - MQOs
  - Radiological holding time (during transport and in the laboratory)
  - Preservation or storage techniques
  - Sample digestion
  - Interferences, both radiological and non-radiological (more or less significant)
  - Turnaround time for results
  - Method bias (see MARLAP Attachment 6A)

10. Evaluating Methods and Laboratories   6

- Does the matrix present any difficulties with regard to the holding times?
- Preservation and storage will need to be identified for each radionuclide in each matrix.
- Does digestion need to occur? (Sometimes not, as for tritium in water or soil.)
- The potential interferents need to be identified like calcium in milk interfering with the strontium analysis (in particular in the gravimetric recovery).
- Once the lab gets the samples, what is their TAT, and does it match your projects needs?
- Has this lab performed this analysis in this matrix before?

TEC & Project Manager decide that the methods proposed by the laboratory are:

- Appropriate
  - Can achieve the MQOs and other APS requirements
- Not appropriate
  - Cannot achieve the MQOs or other APSs

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^{90}Sr Example MQO:

A method uncertainty (u_{MR}) of 0.5 pCi/L or less at 8 pCi/L

	LSC	Beta Detector	GPC	Required for Project
Routine Method Uncertainty (pCi/L)	0.2	1.0	0.3	0.5 (Required Method Uncertainty)

Note: This example is focused on the method uncertainty. Other requirements of the APS should be evaluated.

Laboratory evaluation process follows the evaluation
and approval of the method by the TEC:

- Initial
- Continuing

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Consider:

- Quality manual
- Staff, instrumentation, and facilities
- Prior contract work
- Performance of internal QC program
- Performance in external performance evaluation programs

Continued...

- Does the lab have a quality manual? Does it identify the key elements of a QA program: organizational structure, training requirements, documentation requirements, program goals, personnel qualifications, traceability issues, etc.

- Does the laboratory's size and staff size meet the projects needs? You will be taking 50 samples a week to be analyzed for multiple analytes; The lab has 3 bench personnel – is this a good fit?

- Has the laboratory performed this type of work before especially with regard to TAT, matrix, analyte and volume? Can they produce an analytical report that meets the data needs of the project?

- Ask to review their internal QC program documentation as well as any external QC programs in which they participate.

Continued...

- Is an onsite audit or assessment necessary?
- Can audit reports from other entities be used?
- Performance test/evaluation samples as a pre-award requirement?
- Is the laboratory accredited? By whom?

- It may be possible to obtain audit reports from other agencies.
- Should preference be given to laboratories that have been already audited?

- The method is accepted by the TEC
- The laboratory is approved based on the laboratory's quality program, external audits, staffing, etc.
- Several laboratories may meet the requirements
- The scoring and evaluation scheme* developed will allow the PM to decide which laboratory to select

*See Chapter 5 and Appendix E

An example of a proposal evaluation scheme, taken from MARLAP Table E.6, is in the handouts at Tab 15.

- Project plan should identify the method of ongoing evaluation, using the Statement of Work (SOW) and APS as a quantitative measure:
    - "Desk" audit (using data packages from laboratory)

        and if necessary

    - Onsite audit

- Evaluation of QC samples for all matrices is a major part of either type of audit.

Part of the evaluation process must consider how often is the laboratory **not** producing the results required by the SOW. A single non-compliance for not achieving an MQO is not grounds for immediate change of laboratory.

- Assess performance such as frequency of MQOs not achieved. Is once per batch OK or twice per quarter?
- Does the lab meet the quantitative contract requirements, but not the TAT?
- Are the reports complete or missing laboratory dialogue information?
- Does the lab recognize ongoing bias or routine blank contamination (whether or not significant)?

In the MARLAP process, the criteria for evaluating the batch QC samples are based on the required project specific method uncertainty

- Matrix spike
- Laboratory control sample (LCS)
- Duplicate sample
- Laboratory blank
- Matrix spike duplicate

- This is not a complete list of all QC samples that could be used. Not all QC samples are appropriate for each investigation. Which ones will be selected are part of the APS process.

- Another way of evaluating lab performance is by performance evaluation/testing sample (external program). These samples may be provided by the project or by an independent contractor.

Why Do All These QC samples?

- To help ensure data is of proper quality to support the decision.

- The purpose of trending method uncertainties, LCS, and spike results is to help decide if methods or laboratories need to be changed.

- This is part of the feedback loop for confirmation of performance/improvement in the MARLAP process.

- *...and because the regulators tell you to.*

- Acceptable spiking range
- Method of spiking
- Acceptance criteria (Z score)

- The SOW will specify the acceptable range of activity. It is the responsibility of the project team, TEC or PM to verify the correct activities have been used.

- Method of spiking need not be specified, but should be approved by the TEC.

- The SOW should specify the acceptance criteria so that the laboratory is aware of the quantitative requirements for the project. Acceptable range is based on the "Z-score."

Matrix Spike Requirements for ^{90}Sr in Milk

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

$$Z = \frac{SSR - SR - SA}{0.0625 \times \sqrt{SSR^2 + \max(SR,8)^2}}$$

can be negative

Control limits for Z statistic are ±3

Spike added is 50 pCi/L. Spiked sample result is 57.8 pCi/L. Unspiked sample result is 4 pCi/L. Does this meet the APS requirements?

SSR = spiked sample result

SA = spike activity added

SR = unspiked sample result

Z = [57.8-50.0-4]/{0.0625x[57.8^2 + 8^2]$^{1/2}$}

$\quad$ = 3.8/{0.0625[3.34x10^3 + 64]$^{1/2}$}

$\quad$ = 3.8/{ 0.0625(58.3)} = 1.04

Z value is acceptable

- Usually made in demineralized water matrix for liquids (this would be the case for milk, unless a surrogate, synthetic matrix is specified in the SOW)
- Activity concentration should be near the AL
- The uncertainty of the spike activity used is normally negligible

- Performed for each batch but does not have to have the same activity value each time prepared; monitor the percent difference (%D).
- Activity needs to be measured near the decision level, but the number of accumulated counts should be large enough so that the Poisson counting uncertainty is small. This provides the continued confidence that the method uncertainty is being reproduced at the action level.
- The activity of the spike added should be from a primary standard and thus its uncertainty is negligible when compared to the uncertainty of the measured spiked sample activity.

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

SSR = Spiked sample result

SA = spike activity (or concentration) added

Control limits: ($\pm 3\ \varphi_{MR}$) × 100

Note that limits are in %

Would an LCS value of 12.0 pCi/L be an acceptable result for our example if the LCS Expected value is 10 pCi/L?

- SSR = spiked sample result
- SA = spike activity added
- SR = unspiked sample result
- APS specifies that the LCS concentration will be 10-20 pCi/L and have a spiking uncertainty of ≤5%
- φ_{MR} is the fractional required method uncertainty, u_{MR} / UBGR
- $u_{MR} = \Delta/10 = (8-3) / 10 = 0.5$
- For the ^{90}Sr analysis in our example, $\varphi_{MR} = u_{MR}$ / UBGR = 0.5/8 = 0.0625
- If the LCS is 10 pCi/L, the control limits are 10±1.875 ≈ 19%
- Thus, the LCS value is outside the control limit and will need to be noted appropriately in the validation report (later).

Duplicate Sample

- A second aliquant taken from the original sample container
- Agreement based on a statistical test when average of both samples is within a specified range

aliquant: A representative portion of a homogeneous *sample* removed for the purpose of analysis or other chemical treatment. The quantity removed is not an evenly divisible part of the whole sample. An "aliquot" (a term not used in MARLAP) by contrast, is an evenly divisible part of the whole.

$$\overline{X} = \frac{X_1 + X_2}{2}$$

When $\overline{X} < 8$ the control limit for the absolute difference $| x_1 - x_2 |$ is

$$CL = 4.24\, u_{MR} = 4.24 \times 0.5 = 2.1$$

When $\overline{X} > 8$ the control limit for the *relative percent difference (RPD)* is

$$RPD = 100 \times \frac{| x_1 - x_2 |}{\overline{X}}$$

and the value for the limit is

$$CL = 4.24\, \varphi_{MR} \times 100 = 4.24 \times 0.625 \times 100 = 27\%$$

Duplicate results are obtained on an unknown sample: 14.6 and 17.2 pCi/L. Are they acceptable per our example APS?

$u_{MR} = \Delta/10 = (8\text{-}3) / 10 = 0.5$

$\varphi_{MR} = u_{MR} / UBGR = 0.5 / 8 = 0.0625$

always

For $X_{avg} < 8$ the control limit is:

$$4.24 u_{MR} = 0.5 \times 4.24 = 2.1$$

For $X_{avg} > 8$ the control limit is:

$$RPD = 100 \times 4.24\, \varphi_{MR} = 100 \times 4.24 \times 0.0625 = 26.5\%$$

For the example in this slide:

$$(X_1 + X_2) / 2 = (14.6 + 17.2) / 2 = 15.9 > 8$$

Calculate the RPD =

$$[(x_1 - x_2) / 15.9] \times 100 = 16.4\% < 27\% \text{ OK}$$

Blanks

How are they made?

- Field blank
- Trip blank
- Method blank

Actions if blanks are "positive" for activity?

- Repeat batch analysis?
- Subtract blank value from all results?

- Type of blank must be specified in SOW.
- The "true" blank value is assumed to be "zero." It is expected that there will be a distribution of values around "zero."
- Positive values are ones that exceed the critical level.
- One "positive" blank does not require stopping the process or even repeating an analysis. Evaluate the trend.

Ideally the "true" value is zero. Control chart should have the central line at zero with:

Control limits: $\pm 3\ u_{MR}$

Values plotted on the control chart for trending
No action based on single measurement

Control limit for Sr APS is 1.5 pCi/L (3×0.5 pCi/L), the u_{MR}

- u_{MR} is the required method uncertainty on an <u>absolute</u> basis

- What does it mean if the "value" is outside the control limit at the low end? (i.e., the -3 u_{MR} value is -0.12 and the blank for the batch is -0.16)?

- What is the significance of the Attachment B "preamble" of the APS*?
- Note the specificity of agreement criteria for each of the QC samples.

*See handout at Tab 14

- The batch limit is defined: note that the number per batch *includes* the QC samples. Thus, the number of unknowns is limited to 20-4, or 16. Notice that a single QC, matrix spike, or blank "failure" does not stop the analytical process. However it is incumbent on the laboratory QC manager to stop work when trending indicates a problem.
- Each QC sample has its own equation and acceptance criterion.

EXAMPLE:
QC Requirements - ^{90}Sr in Milk

Blank Results Sr-90 in Milk
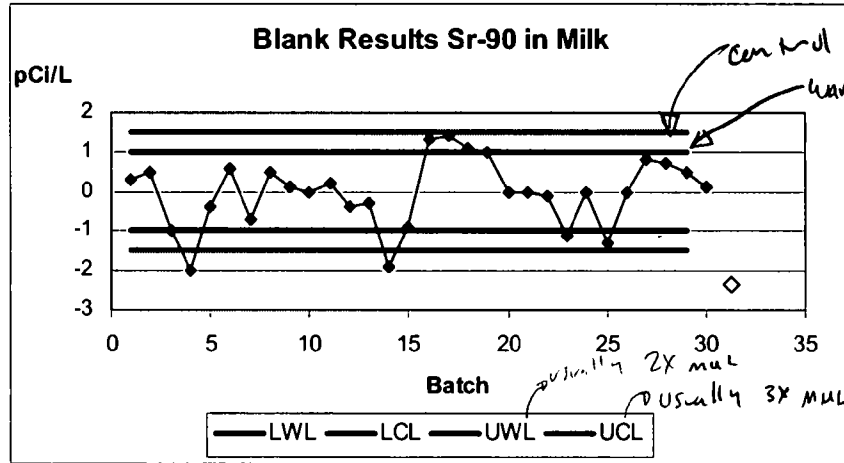
The current value ◇ for your batch is −2.2. OK?

The current value is clearly outside the lower control limit. This will require a notation during the validation and verification process.

This will be addressed later during the workshop.

- Radioanalytical specialist reviews the methods for technical adequacy

- TEC performs an independent calculation of the method's MDC and required method uncertainty (u_{MR}) using laboratory's typical or sample-specific parameters

- PM or TEC evaluates available lab data for bias based on PE testing or samples

- "Z-score" is used for matrix spike evaluation

- An audit team include a radioanalytical specialist

- Handouts identify the results received from the laboratory for the 5 milk samples recently sent by your project (Batch #31) with trend graphs of the QC samples performed by the laboratory for the ^{90}Sr analysis

- Conduct an ongoing evaluation of the laboratory's performance based on this data set

Refer to APS handouts at Tab 14 pages 7-9 for example control charts.

Radiochemical Data Verification and Validation

Module 11

Dave McCurdy

and

Bob Litman

1

- Laboratory conditions and operations are compliant with:
  - SOW
  - Sample analysis plan
  - Quality assurance project plan (QAPP)
- Identifies problems that should be investigated during data validation
- Material delivered by the laboratory in compliance with SOW
- Checks for consistency and *comparability* of the data throughout the data package
- Checks for *completeness* of the results to ensure all necessary documentation is available

- Analytical data *verification* assures laboratory conditions and operations were compliant with the SOW based on project plan documents. The updated project plan documents specify the analytical protocols the laboratory should use to produce data of acceptable quality and the content of the analytical data package.

- Verification compares the analytical data package delivered by the laboratory to these requirements (compliance), and checks for consistency and comparability of the data throughout the data package, correctness of basic calculations, data for basic calculations, and completeness of the results to ensure all necessary documentation is available.

- Compliance verification may include a review of laboratory staff signatures (written or electronic), data and report dates, case narrative reports, sample identifiers, radionuclides and matrices for analyses, methods employed for analyses, preservation of samples, reference/sampling and analysis dates, spectral data, chemical yields, detector-efficiency factors, decay and ingrowth factors, radiological holding times, analytical results, measurement uncertainties, minimum detectable concentrations, daily instrument and batch QC results, etc.

- All these actions are performed after the analysis has been done. How do you ensure that a large percentage of the time that this process establishes usable data? By telling the lab what your requirements are in the SOW!

Focuses on the individual data generated by the
laboratory for each sample and laboratory process:

- Are the data calculation processes and analytical methods *compliant* with the SOW?
- Based on <u>measurable</u> factors
- Verification report presents summary of the process including a single data qualifier (E) if needed

- The data package that the *data verifier* receives from the laboratory must have all the data necessary to perform this function. This means that you first need to know what characteristics of verification your project requires to be performed. The data verification requirements are written down in the QAPP and incorporated in the SOW.

- The "E" qualifier stands for "exception." This indicates that the verifier has found something in the data package which is an exception to the requirements.

- An example of this would be if the sample size or aliquant process is missing from the report documentation.

- Qualifiers (data flags) are discussed later in this module.

Data Verification
(Continued)

Verification will determine whether:

- Correct procedures were used
- All required documentation was included in the laboratory report
- The report conforms to what was required in the SOW (e.g., analytes, MDCs to be achieved, and method uncertainty (u_{MR}) listed, reporting units, calculational process, sample preservation, holding times)?

- Note any exceptions
- All points are described in a *Verification Report*

- Evaluates the data to determine the presence or absence of an analyte
- Establishes the uncertainty of the measurement process
- Qualifies the usability of each datum
  - Compares data produced with the measurement quality objectives and any other analytical process requirements contained in the analytical protocol specifications developed in the planning process.

Data assessment = data verification + data validation + data quality assessment (not covered here)

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

- This process involves the application of qualifiers that reflect the impact of not meeting the MQOs and any other analytical process requirements. Validation then evaluates the data to determine the presence or absence of an analyte, and the uncertainty of the measurement process.

- During validation, the technical reliability and the degree of confidence in reported analytical data are considered.

- The data validator should be a scientist with radiochemistry experience.

Data Validation

Quantitative tests and qualitative inspection for analytical detection and method uncertainty, and review of any exceptions noted from verification report

- Focus moves from individual data compliance with the SOW requirements to overall project MQOs

- Qualitative inspection of alpha, gamma, or LSC spectra for proper energy selection, interference corrections, etc.
- In some cases, from the spectral data provided, the reviewer can quantify or estimate the magnitude of the interferences and determine of the lab corrected the results appropriately.

Validation will:

- Review verification exceptions ("E" designations) and determine if further qualifiers are needed
- Determine if the analytical measurement system was in statistical control
- Determine if MQOs were achieved
- Apply quantitative tests for the QC (or PE) samples to assess their validity
- Determine if recent lab procedure changes affect applicability to matrix or analyte
- Apply additional qualifiers to data based on tests

• All points are described in a *Validation Report*

The quantitative measures that will be used are:

• Have the MQOs been achieved for the methods used?

• Have the QC samples met the requirements (for uncertainty and method detection) of the QAPP?

- Project Manager assigns data verifier and validator
  - Generally performed by different people (for cross-checking)
- Project validation plan developed and in place prior to data Verification and Validation
- Validation plan incorporates input from all stakeholders.
  - Should be part of initial planning process
  - Integral part of project plan documents

Validation plan should be part of the initial planning process and an integral part of the project plan documents. May be stand-alone document or part of another QC document.

The data validation plan should contain the following information:

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

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

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

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

Plan (developed from the SOW and APS) includes the specific tests and limits to be used by the validator:

- Tables indicating the MDC, critical level, MQC, required method uncertainty (u_{MR}), and how they are to be calculated
- Acceptance criteria for duplicates, spikes, QC and blanks, and how they are to be calculated
- Which data qualifiers (8.3.3) are to be used and under what circumstances
- The percent of the raw data required to be reviewed (>0)

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Data Verification and Validation Process
(8.5)

Four Stages:

1. Sample handling and analysis system
2. QC sample requirements meet specified MQOs
3. Tests of detection and unusual uncertainty
4. Final data qualifiers are affixed to the individual datum

Direct evidence of the sampled material being properly analyzed is necessary:

1. Identification
2. Analysis and method
3. Complete reporting
4. Chain of custody
5. Sample size
6. Preservation
7. Validity of QC samples and results
8. Analysis requirements

11. Data Verification and Validation   11

- Sample name and lab ID number
- Analyte analyzed and identification of method used.
- Complete reporting of required analytical parameters such as concentration, combined standard uncertainty (CSU), critical level (CL), minimum detectable concentration (MDC), proper reporting units, radiological holding time (RHT), turnaround time (TAT), decay and ingrowth times, etc.
- Unbroken COC indicating correct sample date: dates of collection, receipt, analysis, reporting.
- Appropriate sample aliquant is used.
- Preservation of sample is properly performed and maintained while at laboratory awaiting analysis.
- All QC samples required by the SOW/APS were used. The standards were in the proper concentration range and were not expired.
- Specific analytical requirements for accuracy and precision were achieved (FWHM, self shielding, yield, dilution factors, count time, etc.).

These apply both to verification and validation.

QC Samples
(8.5.2)

Evidence of all QC results (indexed to the samples in a batch) should accompany the laboratory report:

- Were the types of QC samples specified in the SOW used?

- Were the correct number of QC samples per batch size used?

- Do any of the QC sample results **require** a data qualifier to be added to the sample results?

The word require is very important. This is a qualitative decision to be made by the validator. The result of a single QC being beyond the project control limit for one radionuclide *does not necessarily* cause the data set for that radionuclide to receive an "R" data qualifier. What does the history (i.e., trend graph) for this parameter reveal?

Effective data validation must include:

- Use of an approved, pre-established data validation plan
  and
- A data package that has been verified to contain the essential elements required for validation

- The laboratory needs to know how the data will be evaluated, so they can attempt compliance.
- If the data package is not compliant, the validator is stuck!

E – Indicates that an exception or non-compliance has occurred. Examples of when this qualifier would be added include:

- Documentation absent from the data package
- Sample analysis radiological holding time not met
- Different procedure or unqualified analyst was used
- Calculation of concentration is not in accordance with SOW
- Several other non-compliances are possible

The "E" qualifier may be changed or eliminated during the validation process

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U: Analytical result is < **critical value**; a non-detect

Q: A reported measurement uncertainty that exceeds the required method uncertainty or relative method uncertainty (φ_{MR} or u_{MR})

J: A result that is unusually uncertain or estimated

R: A result that is rejected due to severe data problems

- These qualifiers are used for individual <u>sample</u> results.
- "J" qualifier is not based on the reported measurement uncertainty but is based on the <u>J</u>udgment of the validator; for example the uncertainty reported is underestimated or not clearly determined by the laboratory.
- The critical value should be based on the 1σ uncertainty of the individual measurement. It may be between 1.5 and 2.0 times the 1σ standard deviation of the count rate (except when zero). Further discussion of the critical level is given in Attachment 3B to Chapter 3 in MARLAP on analyte detection (provided behind Tab 13).

S(+/-): A LCS, MS or MSD which is above (+) or below (-) the upper or lower control limit

P: A sample result with its duplicate(replicate) that exceeds a control limit

B(+/-): A blank result that is outside the upper (+) or lower (-) control limit

These are qualifiers that are assigned to the <u>samples</u> based on the results of <u>QC samples</u> in the data set.

Convention used for data validation qualifiers:

- If a sample result is above the project reporting concentration (usually the critical level)

    NO QUALIFIER IS USED FOR DETECTION

- If all parameters associated with the sample measurement, and its associated QC samples are satisfactory

    NO QUALIFIER IS USED

If there are no symbols in the data qualifier column, there is detectable activity that is validated and verified.

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Required Method Uncertainty

Used two ways in verification and validation:

- For individual data points, if the reported measurement uncertainty is greater than the required method uncertainty (u_{MR} or φ_{MR}), append data qualifier "**Q**" to the data

- In equations for QC, blanks, duplicates, and spikes to set up acceptance criteria

Data validator should determine if:

- The critical level has **not** been exceeded, then the "U" qualifier should be assigned

- The "Q" qualifier should be used when the reported measurement uncertainty is greater than the required method uncertainty

Is it required for the analyte for each sample, or is an aggregate agreement with the required minimum detectable concentration (RMDC) satisfactory? This would be a project specific requirement, BUT note that MARLAP recommends that the MDC be sample specific.

Data rejection ("R") should be a rare occurrence

Three possible reasons to reject data are:

1. Insufficient or incorrect data supporting results/ documentation are available

2. Assumptions made in the planning process regarding the applicability of the method to the analysis are not true

3. High level of uncertainty ascribed to the datum

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1. The laboratory cannot supply, or cannot supply in a timely manner all the information needed to verify that the data is correctly calculated or the proper procedures were followed during the life of the sample at the lab.

2. The planning process assumed that all samples would be completely dissolved by the lab method used. The lab reports that there was an insoluble residue. The planning assumption does not meet the sample analytical results. The data thus produced are not valid and would be qualified with an "R" qualifier. This is an example of where the **MARLAP process feedback** loop is essential. The insoluble residue was unexpected and thus requires investigation into the sample dissolution process and potentially the method being used. This would likely invovle a change to the APS.

3. This is known at all other levels as "Other (fill in the reason)."

Validation Report
(8.6)

Summarizes the validation process and its conclusions. Includes:

- Either a narrative or table summarizing exceptional circumstances regarding the validation tests
- List of samples whose results have been validated with the laboratory and client identifiers
- Summary of all validated results with associated uncertainty and final data qualifiers
  - Actual values to be reported not an LLD or "<" value
- Summary of the QC sample performance and any potential effect on the validated data

- A summary of exceptional circumstances during the sampling or analysis.
- A list of validated samples with both the project and laboratory identifications.
- A summary of the validated results with the associated uncertainty for each sample.
- A summary of QC sample performance and any effect this may have on the qualifiers ascribed to any datum.

For Matrix Spikes

Calculate the Z statistic for each spike as follows:

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

plot the Z value for each matrix spike on a control chart with:

Control Limits $= \pm 3$

For Duplicates

$$\overline{X} = \frac{X_1 + X_2}{2}$$

If X < AL, the control limit for the absolute difference $|x_2 - x_1|$ is 4.24 u_{MR}

If X > AL, the control limit for the relative percent difference:

$$RPD = 100 \times \frac{|x_1 - x_2|}{\overline{X}}$$

$$= 100 \times 4.24 \, \varphi_{MR}$$

Continued...

The example for duplicates is taken from the Sr APS handout in Tab 14.

$u_{MR} = \Delta/10 = [8-3]/10 = 0.5$

$\varphi_{MR} = u_{MR}/UBGR = 0.5/8 = 0.0625$

For ^{90}Sr matrix spike:

$Z = (15.5-20.0-1.55) / \{0.0625 \times [15.5^2 + 8^2]^{1/2}\}$

$\quad = -6.05 / \{0.0625 \times [240.25 + 64]^{1/2}\}$

$\quad = -6.05 / \{0.0625 \times 17.44\}$

$\quad = -5.55$

For matrix spike samples outside the control limits, the qualifier "S" should be used with a "+" or "–" (above or below) indicating direction of discrepancy. For this example, S- would be the qualifier attributed to each of the samples (but not to the matrix spike itself).

^{90}Sr example duplicates:

For $X_{avg} < 8$, the control limit is

$\quad$ 4.24 $u_{MR} = 0.5 \times 4.24 = 2.1$

The absolute value for the two samples is used or $|1.61 - 1.95| = 0.34$

Since this is less than 2.1 the duplicate result is satisfactory, and no qualifier would be used for the samples for this result.

If the X_{avg} was > 8, the control limit would be

$\quad$ RPD = 100 × 4.24 φ_{MR} = 100 × 4.24 × 0.0625 = 26.5%

For Blanks

Plot the values for all blanks on a control chart with:

Control Limits = ±3 u_{MR}

For LCS

Calculate the %D from the data as follows:

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

And plot the %D for all LCS on a control chart with:

Control Limits = (±3 φ_{MR}) × 100

For this example, the control limit for the blank = ±3 × 0.5 = ±1.5.

The value of the blank is -0.43, it falls within the control limit: No qualifier is necessary.

For blank samples that are outside the control limits, the qualifier "B" should be used with a "+" or "–" (above or below) to all the samples in the batch.

For this example, blank %D = ±3 × 0.0625 × 100 = 18.75%.

For the LCS %D = {(12.8-10) / 10} × 100 = 28%: the sample is outside the control limits.

For LCS samples that are outside the control limits, the qualifier "S" should be used with a "+" or "–" (above or below) to all the samples in the batch. In this case, "S+" would be applied to all samples.

Turn to Tab 14...

- Review quality control graphs
- Review data validation process

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MARLAP Recommends ...

- Project objectives, implementation activities, and QA/QC data be well-documented in the project plans
- Calibration be addressed in a quality system and through an audit (demonstration of calibration may be required as part of the project deliverables)
- Assessment criteria be established in the directed planning process and stated in the project plan documents
- Results of each measurement, expanded measurement uncertainty, critical level for each sample, and the analyte/sample-specific MDC be reported for each sample
- Any analyte for which the final measurement is less than the critical level be qualified with a U for "undetected"

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Turn to Tab 21 for the laboratory report from Lab XYZ concerning ^{241}Am by alpha spectrometry in the ground water samples

The principal MQOs in any project will be defined by:

- The *required method uncertainty*, u_{MR}, below the *action level*

    AND

- The *relative method uncertainty*, φ_{MR}, above the *action level*

$$\varphi_{MR} = u_{MR} / AL$$

When making decisions about *individual samples* . . . . $u_{MR} \sim \Delta/3$

When making decisions about the *mean of several samples* . . $u_{MR} \sim \Delta/10$

Where Δ is the width of the gray region . . . . $\Delta = AL - DL$

Method Uncertainty: MARLAP's Common Thread

Definition:
- Predicted uncertainty of a measured value that would likely result from the analysis of a sample at a specified analyte concentration.
- Combines *imprecision* and *bias* into a single parameter whose interpretation does not depend on context.

MARLAP recommends:
- Identify the method uncertainty at a specified concentration (typically the *action level*) as an important method performance characteristic.
- Establish a measurement quality objective for method uncertainty for each analyte/matrix combination.

MQO for the method uncertainty (at a specified concentration):
- Links the three phases of the data life cycle: planning, implementation, and assessment.
- 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 <u>action level</u>, and the lower bound is termed the "<u>discrimination limit</u>."

Examples of MQOs for method uncertainty at a specified concentration:
- A method uncertainty of 0.01 Bq/g or less is required at the action level of 0.1 Bq/g.
- The method must be able to quantify the amount of ^{226}Ra present, given elevated levels of ^{235}U in the samples.

Terminology:
u_{MR}	Required method uncertainty (absolute)
$\varphi_{MR} = u_{MR} / AL$	Required method uncertainty (relative)
$\Delta = AL - DL$	Width of the gray region (range of values where the consequences of a decision error are relatively minor)
Action level	Concentration that will cause a decisionmaker to choose one of the alternative actions
Discrimination limit	Synonymous with the lower bound of the gray region

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The MARLAP Process

Directed Planning Process (Chapter 2)
- Key Analytical Issues (Chapter 3)
- Development of Analytical Protocol Specifications
- Includes MQOs (Chapter 3)

↓

Develop Plan Documents that Incorporate Analytical Protocol Specifications (Chapter 4)
(e.g., QAPP, SAP, Data Validation Plan)

↓

Development of SOW (Chapter 5)
- Includes Analytical Protocol Specifications (MQOs)

Planning Phase

↓

Laboratory Responds with Analytical Protocols
(Chapter 6)
- Selected to Meet Requirements of Analytical Protocol Specifications
- Performance Data Provided

↓

Initial Evaluation of Analytical Protocols and Laboratory
(Chapter 7)
- Review of Performance Data
- Performance Evaluation (PE) Samples/Certified Reference Materials (CRMs) Analyzed
- Quality Systems Audit

→ **Project Manager**   Protocols Rejected

Protocols Accepted

↓

Update Plan Documents
(Chapter 4)
- Include or Reference Accepted Analytical Protocols

Start Analysis of Samples

↓

Ongoing Evaluation of Laboratory Performance
(Chapter 7)
- Evaluation of QC and PE Sample Results
- Laboratory Audits
- Evaluation of Sample-Specific Parameters (i.e., yield)

→ **Project Planning Team**   Corrective Actions

Implementation Phase

Analyses Completed

↓

Data Evaluation and Assessment
- Data Verification (Chapter 8)
- Data Validation (Chapter 8)
- Data Quality Assessment (Chapter 9)

Assessment Phase

↓

Data of Known Quality for Decisionmaking

The Key to the MARLAP Process

The principal MQOs in any project will be defined by:

- The *required method uncertainty*, u_{MR}, below the *action level*

  AND

- The *relative method uncertainty*, φ_{MR}, above the *action level*

$$\varphi_{MR} = u_{MR}/AL$$

When making decisions about *individual samples* . . . . $u_{MR} \sim \Delta/3$

When making decisions about the *mean of several samples* . . $u_{MR} \sim \Delta/10$

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MQO for the method uncertainty (at a specified concentration):
- Links the three phases of the data life cycle: planning, implementation, and assessment.
- 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 <u>action level</u>, and the lower bound is termed the "<u>discrimination limit</u>."

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- A method uncertainty of 0.01 Bq/g or less is required at the action level of 0.1 Bq/g.
- The method must be able to quantify the amount of ^{226}Ra present, given elevated levels of ^{235}U in the samples.
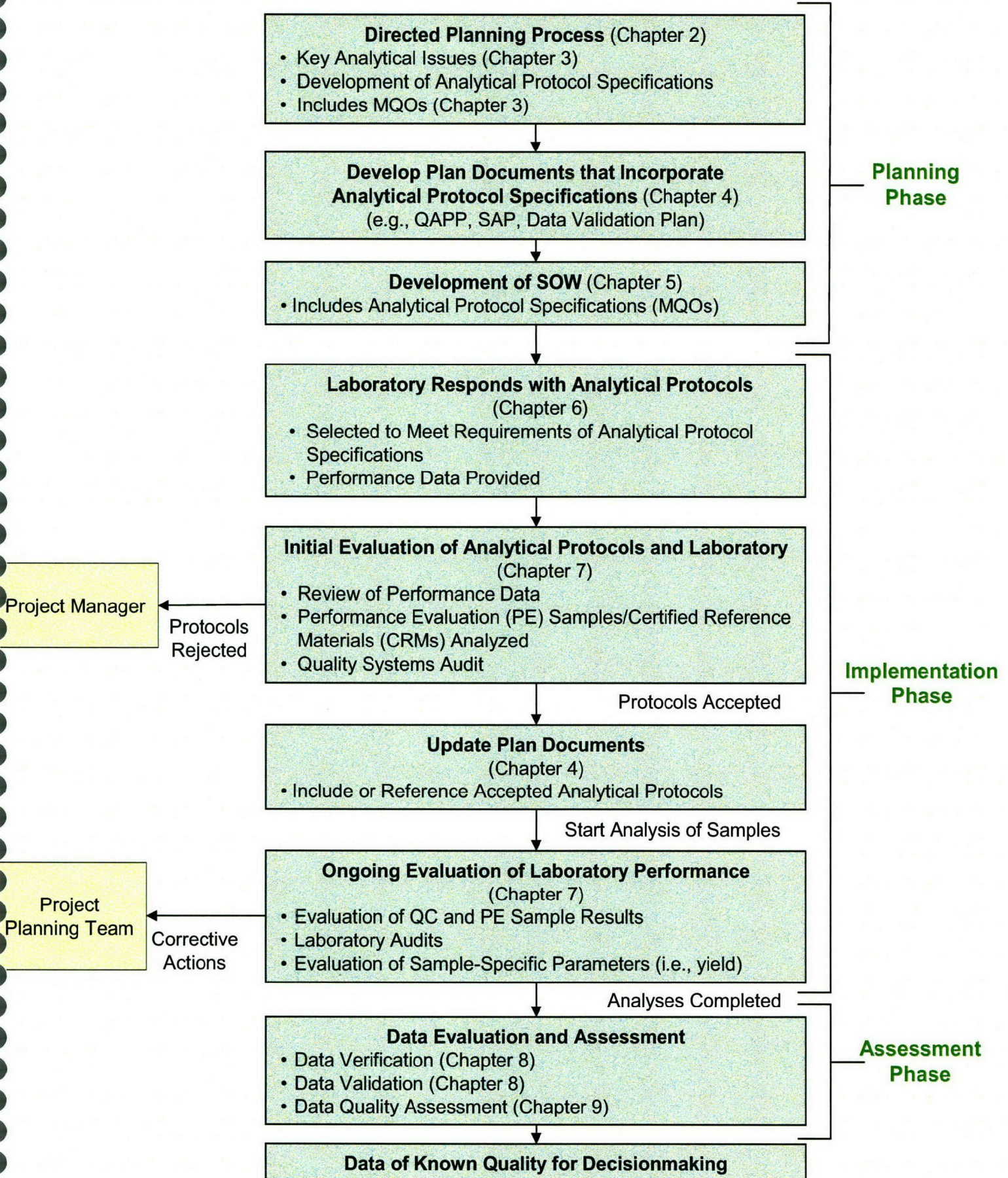
Terminology:
u_{MR}	Required method uncertainty (absolute)
$\varphi_{MR} = u_{MR}/AL$	Required method uncertainty (relative)
$\Delta = AL - DL$	Width of the gray region (range of values where the consequences of a decision error are relatively minor)
Action level	Concentration that will cause a decisionmaker to choose one of the alternative actions
Discrimination limit	Synonymous with the lower bound of the gray region

III. SPECIFY A RANGE OF CONCENTRATIONS WHERE THE CONSEQUENCES OF DECISION ERRORS ARE RELATIVELY MINOR

The gray region, or region of uncertainty, indicates an area where the consequences of a Type II decision error are relatively minor. It may not be reasonable to attempt to control decision errors within the gray area. The resources expended to distinguish small differences in concentration could well exceed the costs associated with making the decision error.

In this example, the question is whether it would really make a major difference in the action taken if the concentration is called 30 pCi/g when the true value is 26 or even 22 pCi/g. If not, the gray region might extend from 20 to 30 pCi/g . This is shown in Figure B.5.

The width of the gray region reflects the decisionmaker's concern for Type II decision errors near the action level. The decisionmaker should establish the gray region by balancing the resources needed to "make a close call" versus the consequences of making a Type II decision error. The cost of collecting data sufficient to distinguish small differences in concentration could exceed the cost of making a decision error. This is especially true if the consequences of the error are

judged to be minor.

There is one instance where the consequences of a Type II decision error might be considered major. That is when expensive remediation actions could be required that are not necessary to protect public health. It could be argued that this is always the case when the true concentration is less than the action level. On the other hand, it can be also be argued that remediation of concentrations near, even though not above the action level, will still carry some benefit. To resolve the issue,

FIGURE B.5 — The gray region is a specified range of values of the true concentration where the consequences of a decision error are considered to be relatively minor

however, the project planning team knows that not all values of the average concentration below the action level are equally likely to exist in the survey unit. Usually, there is some knowledge, if only approximate, of what the average value of the concentration in the survey unit is. This information can be used to set the width of the gray region. If the planning team is fairly confident that the concentration is less than 20 pCi/g but probably more than 10 pCi/g, they would be concerned about making Type II errors when the true concentration is between 10 and 20 pCi/g. However, they will be much less concerned about making Type II errors when the true concentration is between 20 and 30 pCi/g. This is simply because they do not believe that the true concentration is likely to be in that range. Figure B.6 shows three possible ways that the project planning team might decide to set the gray region. In "A" the project planning team believes the true concentration remaining in the survey unit is about 15 pCi/g, in "B" they believe it to be about 20 pCi/g, and in "C" about 25 pCi/g. In each case, they are less concerned about a decision error involving a true concentration greater than what is estimated to actually remain. They have used

FIGURE B.6 — Three possible ways of setting the gray region. In (A) the project planning team believes the true concentration remaining in the survey unit is about 15 pCi/g, in (B) about 20 pCi/g and in (C) about 25 pCi/g

their knowledge of the survey unit to choose the range of concentration where it is appropriate to expend resources to control the Type II decision error rate. The action level, where further remediation would be necessary, defines the upper bound of the gray region where the probability of a Type I error should be limited. The lower bound of the gray region defines the concentration below which remediation should not be necessary. Therefore, it defines where the probability of a Type II error that would require such an action should be limited.[2]

IV. ASSIGN TOLERABLE PROBABILITY VALUES FOR THE OCCURRENCE OF DECISION ERRORS OUTSIDE OF THE RANGE SPECIFIED IN III

As part of the DQO process, the decisionmaker and planning team must work together to identify possible consequences for each type of decision error. Based on this evaluation, desired limits on the probabilities for making decision errors are set over specific concentration ranges. The risk associated with a decision error will generally be more severe as the value of the concentration moves further from the gray region. The tolerance for Type I errors will decrease as the concentration increases. Conversely, the tolerance for Type II errors will decrease as the concentration deceases.

In the example, the decisionmaker has identified 20–30 pCi/g as the area where the consequences of a Type II decision error would be relatively minor. This is the gray region. The tolerable limits on Type I decision errors should be smallest for cases where the decisionmaker has the greatest concern for making an incorrect decision. This will generally be at relatively high values of the true concentration, well above the action level. Suppose, in the example, that the decisionmaker is determined to be nearly 99 percent sure that the correct decision is made, namely, *not* to reject the null hypothesis, *not* to release the survey unit, if the true concentration of radionuclide *X* is 40 pCi/g or more. That means the decisionmaker is only willing to accept a Type I error rate of roughly 1 percent, or making an incorrect decision 1 out of 100 times at this concentration level. This is shown in Figure B.7(a).

If the true concentration of *X* is closer to the action level, but still above it, the decisionmaker wants to make the right decision, but the consequences of an incorrect decision are not considered as severe at concentrations between 30 and 40 pCi/g as they are when the concentration is over 40 pCi/g. The project planning team wants the correct action to be taken at least 90 percent of the time. They will accept an error rate not worse than about 10 percent. They will only accept a data collection plan that limits the potential to incorrectly decide not to take action when it is actually needed to about 1 in 10 times. This is shown in Figure B.7(b).

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[2] Had the null hypothesis been chosen differently, the ranges of true concentration where Type I and Type II errors occur would have been reversed.

The decisionmaker and project planning team are also concerned about wasting resources by cleaning up sites that do not represent any substantial risk. Limits of tolerable probability are set low for extreme Type II errors, i.e. failing to release a survey unit when the true concentration is far below the gray region and the action level. They want to limit the chances of deciding to take action when it really is not needed to about 1 in 20 if the true concentration is less than 10 pCi/g. This is shown in Figure B.7(c).
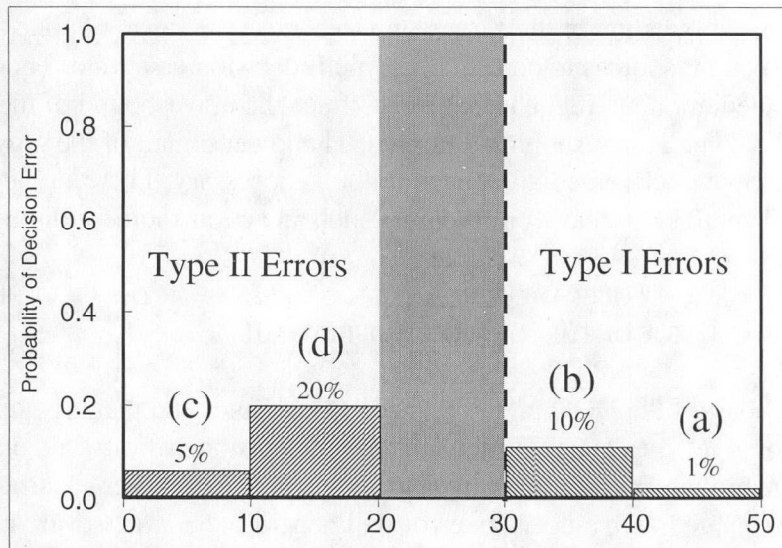
FIGURE B.7 — Example decision performance goal diagram

They are more willing to accept higher decision error rates for concentrations nearer to the gray region. After all, there is some residual risk that will be avoided even though the concentration is below the action level. A Type II error probability limit of 20 percent in the 10–20 pCi/g range is agreed upon. They consider this to be an appropriate transition between a range of concentrations where Type II errors are of great concern (<10 pCi/g) to a range where Type II errors are of little concern. The latter is, by definition, the gray region, which is 20–30 pCi/g in this case . The chance of taking action when it is not needed within the range 10–20 pCi/g is set at roughly 1 in 5. This is shown in Figure B.7(d).

Once the limits on both types of decision error rates have been specified, the information can be displayed on a decision performance goal diagram, as shown in Figure B.7, or made into a decision error limits table, as shown in Table B.3. Both are valuable tools for visualizing and evaluating proposed limits for decision errors.

TABLE B.3 — Example decision error limits table

True Concentration	Correct Decision	Tolerable Probability of Making a Decision Error
0 – 10 pCi/g	Does not exceed	5%
10 – 20 pCi/g	Does not exceed	20%
20 – 30 pCi/g	Does not exceed	gray region: decision error probabilities not controlled
30 – 40 pCi/g	Does exceed	10%
40 – 50 pCi/g	Does exceed	1%

There are no fixed rules for identifying at what level the decisionmaker and project planning team should be willing to tolerate the probability of decision errors. As a guideline, as the possible true values of the parameter of interest move closer to the action level, the tolerance for decision errors usually increases. As the severity of the consequences of a decision error increases, the tolerance decreases.

The ultimate goal of the DQO process is to identify the most resource-effective study design that provides the type, quantity, and quality of data needed to support defensible decisionmaking. The decisionmaker and planning team must evaluate design options and select the one that provides the best balance between cost and the ability to meet the stated DQOs.

A statistical tool known as an estimated power curve can be extremely useful when investigating the performance of alternative survey designs. The probability that the null hypothesis *is* rejected when it *should* be rejected is called the statistical power of a hypothesis test. It is equal to one minus the probability of a Type II error $(1-\beta)$. In the example, the null hypothesis is false whenever the true concentration is less than the action level. Figure B.8 shows the power diagram constructed from Figure B.7 by replacing the desired limits on Type II error probabilities, β, with the power, $1-\beta$. The desired limits on Type I error probabilities, α, are carried over without modification, as is the gray region. Drawing a smooth decreasing function through the desired limits results in the desired power curve. A decision performance goal diagram with an estimated power curve can help the project planning team visually identify information about a proposed study design.
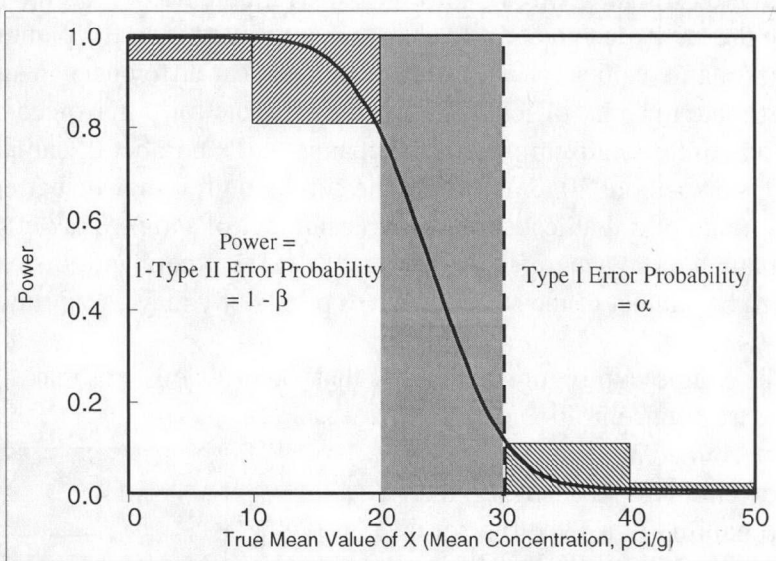
FIGURE B.8 — A power curve constructed from the decision performance goal diagram in Figure B.7

Statisticians can determine the number of measurements needed for a proposed survey design from four values identified on the decision performance goal diagram:

(1) The tolerable limit for the probability of making Type I decision errors, α, at the action level AL).

(2) The tolerable limit for the probability of making Type II decision errors, β, along the

lower bound of the gray region (LBGR).

(3) The width of the gray region, $\Delta = AL - LBGR$, where the consequences of Type II decision errors are relatively minor.

(4) The statistical expression for the total expected variability of the measurement data in the survey unit, σ.

The actual power curve for the statistical hypothesis test can be calculated using these values, and can be compared to the desired limits on the probability of decision errors.

The estimated number of measurements required for a proposed survey design depends heavily on the expected variability of the measurement data in the survey unit, σ. This may not always be easy to estimate from the information available. However, the impact of varying this parameter on the study design is fairly easy to determine during the planning process. Examining a range of reasonable values for σ may not result in great differences in survey design. If so, then a crude estimate for σ is sufficient. If not, the estimate for σ may need to be refined, perhaps by a pilot study of 20 to 30 samples. If the change in the number of samples (due to refining the estimate of σ) is also about 20 to 30 in a single survey unit, it may be better to simply use a conservative estimate of σ that leads to the larger number of samples rather than conduct a pilot study to obtain a more accurate estimate of σ. On the other hand, if several or many similar survey units will be subject to the same design, a pilot study may be worthwhile.

The example in Figure B.9 shows that the probability of making a decision error for any value of the true concentration can be determined at any point on the power curve. At 25 pCi/g, the probability of a Type II error is roughly 45–50 percent. At 35 pCi/g, the probability of a Type I error is roughly 3 percent.

The larger the number of samples required to meet the stated DQOs, the greater the costs of sampling and analysis for a proposed plan. Specifying a narrow gray region and/or very small limits on decision error probabilities indicate a high level of certainty is needed and a larger number of samples will be required.
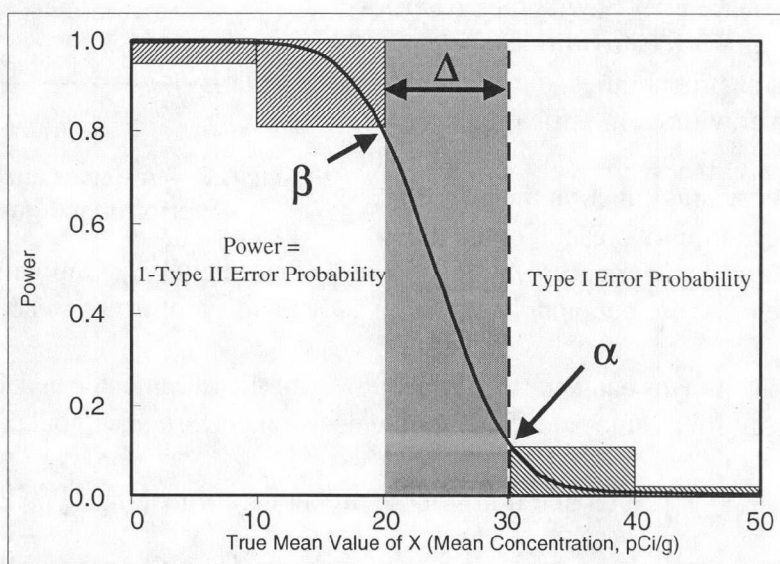
FIGURE B.9 — Example power curve showing the key parameters used to determine the appropriate number of samples to take in the survey unit

Specifying a wide gray region and/or larger limits on decision error probabilities indicates a lower level of certainty is required. A smaller number of samples will be necessary. The required level of certainty should be consistent with the consequences of making decision errors balanced against the cost in numbers of samples to achieve that level of certainty.

If a proposed survey design fails to meet the DQOs within constraints, the decisionmaker and planning team may need to consider:

- ADJUSTING THE ACCEPTABLE DECISION ERROR RATES. For example, the decisionmaker may be unsure what probabilities of decision error are acceptable. Beginning with extremely stringent decision error limits with low risk of making a decision error may require an extremely large number of samples at a prohibitive cost. After reconsidering the potential consequences of each type of decision error, the decisionmaker and planning team may be able to relax the tolerable rates.

- ADJUST THE WIDTH OF THE GRAY REGION. Generally, an efficient design will result when the relative shift, Δ/σ, lies between the values of 1 and 3. A narrow gray region usually means that the proposed survey design will require a large number of samples to meet the specified DQOs. By increasing the number of samples, the chances of making a Type II decision error is reduced, but the potential costs have increased. The wider the gray region, the less stringent the DQOs. Fewer samples will be required, costs will be reduced but the chances of making a Type II decision error have increased. The relative shift, Δ/σ, depends on the width of the gray region, Δ, and also on the estimated data variability, σ. Better estimates of either or both may lead to a more efficient survey design. In some cases it may be advantageous to try to reduce σ by using more precise measurement methods or by forming more spatially homogeneous survey units, i.e. adjusting the physical boundaries of the survey units so that the anticipated concentrations are more homogeneous with them.

APPENDIX C
MEASUREMENT QUALITY OBJECTIVES
FOR METHOD UNCERTAINTY AND
DETECTION AND QUANTIFICATION CAPABILITY

C.1 Introduction

This appendix expands on issues related to measurement quality objectives (MQOs) for several method performance characteristics which are introduced in Chapter 3, *Key Analytical Planning Issues and Developing Analytical Protocol Specifications*. Specifically, this appendix provides the rationale and guidance for establishing project-specific MQOs for the following method performance characteristics: method uncertainty, detection capability and quantification capability. In addition, it provides guidance in the development of these MQOs for use in the method selection process and guidance in the evaluation of laboratory data based on the MQOs. Section C.2 is a brief overview of statistical hypothesis testing as it is commonly used in a directed planning process, such as the Data Quality Objectives (DQO) Process (EPA, 2000). More information on this subject is provided in Chapter 2, *Project Planning Process* and Appendix B, *The Data Quality Objectives Process*. Section C.3 derives MARLAP's recommended criteria for establishing project-specific MQOs for method uncertainty, detection capability, and quantification capability. These criteria for method selection will meet the requirements of a statistically based decision-making process. Section C.4 derives MARLAP's recommended criteria for evaluation of the results of quality control analyses by project managers and data reviewers (see also Chapter 8, *Radiochemical Data Verification and Validation*).

It is assumed that the reader is familiar with the concepts of measurement uncertainty, detection capability, and quantification capability, and with terms such as "standard uncertainty," "minimum detectable concentration," and "minimum quantifiable concentration," which are introduced in Chapter 1, *Introduction to MARLAP*, and discussed in more detail in Chapter 20, *Detection and Quantification Capabilities*. MARLAP also uses the term "method uncertainty" to refer to the predicted uncertainty of the result that would be measured if the method were applied to a hypothetical laboratory sample with a specified analyte concentration. The method uncertainty is a characteristic of the analytical method and the measurement process.

C.2 Hypothesis Testing

Within the framework of a directed planning process, one considers an "action level," which is the contaminant concentration in either a population (e.g., a survey unit) or an individual

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item (e.g., a laboratory sample) that should not be exceeded. Statistical hypothesis testing is used to decide whether the actual contaminant concentration, denoted by X, is greater than the action level, denoted by AL. For more information on this topic, see EPA (2000), MARSSIM (2000), NRC (1998), or Appendix B of this manual.

In hypothesis testing, one formulates two hypotheses about the value of X, and evaluates the measurement data to choose which hypothesis to accept and which to reject.[1] The two hypotheses are called the *null hypothesis* H_0 and the *alternative hypothesis* H_1. They are mutually exclusive and together describe all possible values of X under consideration. The null hypothesis is presumed true unless the data provide evidence to the contrary. Thus the choice of the null hypothesis determines the burden of proof in the test.

Most often, if the action level is not zero, one assumes it has been exceeded unless the measurement results provide evidence to the contrary. In this case, the null hypothesis is H_0: $X \geq$ AL and the alternative hypothesis is H_1: $X <$ AL. If one instead chooses to assume the action level has not been exceeded unless there is evidence to the contrary, then the null hypothesis is H_0: $X \leq$ AL and the alternative hypothesis is H_1: $X >$ AL. The latter approach is the only reasonable one if AL = 0, because it is virtually impossible to obtain statistical evidence that an analyte concentration is exactly zero.

For purposes of illustration, only the two forms of the null hypothesis described above will be considered. However, when AL > 0, it is also possible to select a null hypothesis that states that X does not exceed a specified value less than the action level (NRC, 1998). Although this third scenario is not explicitly addressed below, the guidance provided here can be adapted for it with few changes.

In any hypothesis test, there are two possible types of decision errors. A *Type I* error occurs if the null hypothesis is rejected when it is, in fact, true. A *Type II* error occurs if the null hypothesis is not rejected when it is false.[2] Since there is always measurement uncertainty, one cannot eliminate the possibility of decision errors. So instead, one specifies the maximum Type I decision error rate α that is allowable when the null hypothesis is true. This maximum usually occurs when $X =$ AL. The most commonly used value of α is 0.05, or 5 %. One also chooses another concentration, denoted here by DL (the "discrimination limit"), that one wishes to be able to distinguish reliably from the action level. One specifies the maximum Type II decision error rate

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[1] In hypothesis testing, to "accept" the null hypothesis only means not to reject it, and for this reason many statisticians avoid the word "accept" in this context. A decision not to reject the null hypothesis does not imply the null hypothesis has been shown to be true.

[2] The terms "false positive" and "false negative" are synonyms for "Type I error" and "Type II error," respectively. However, MARLAP deliberately avoids these terms here, because they may be confusing when the null hypothesis is an apparently "positive" statement, such as $X \geq$ AL.

β that is allowable when $X = $ DL, or, alternatively, the "power" $1 - \beta$ of the statistical test when $X = $ DL. The *gray region* is then defined as the interval between the two concentrations AL and DL.

The gray region is a set of concentrations close to the action level, where one is willing to tolerate a Type II decision error rate that is higher than β. For concentrations above the upper bound of the gray region or below the lower bound, the decision error rate is no greater than the specified value (either α or β as appropriate). Ideally, the gray region should be narrow, but in practice, its width is determined by balancing the costs involved, including the cost of measurements and the estimated cost of a Type II error, possibly using prior information about the project and the parameter being measured.

If H_0 is $X \geq$ AL (presumed contaminated), then the upper bound of the gray region is AL and the lower bound is DL. If H_0 is $X \leq$ AL (presumed uncontaminated), then the lower bound of the gray region is AL and the upper bound is DL. Since no assumption is made here about which form of the null hypothesis is being used, the lower and upper bounds of the gray region will be denoted by LBGR and UBGR, respectively, and not by AL and DL. The width of the gray region (UBGR − LBGR) is denoted by Δ and called the *shift* or the required *minimum detectable difference* in concentration (EPA, 2000; MARSSIM, 2000; NRC, 1998). See Appendix B, *The Data Quality Objectives Process*, for graphical illustrations of these concepts.

Chapter 3 of MARLAP recommends that for each radionuclide of concern, an action level, gray region, and limits on decision error rates be established during a directed planning process. Section C.3 presents guidance on the development of MQOs for the selection and development of analytical protocols. Two possible scenarios are considered. In the first scenario, the parameter of interest is the mean analyte concentration for a sampled population. The question to be answered is whether the population mean is above or below the action level. In the second scenario a decision is to be made about individual items or specimens, and not about population parameters. This is the typical scenario in bioassay, for example. Some projects may involve both scenarios. For example, project planners may want to know whether the mean analyte concentration in a survey unit is above an action level, but they may also be concerned about individual samples with high analyte concentrations.

C.3   Development of MQOs for Analytical Protocol Selection

This section derives MARLAP's recommendations for establishing MQOs for the analytical protocol selection and development process. Guidance is provided for establishing project-specific MQOs for method uncertainty, detection capability, and quantification capability. Once selected, these MQOs are used in the initial, ongoing, and final evaluations of the protocols. MARLAP considers two scenarios and develops MQOs for each.

SCENARIO I: A Decision Is to Be Made about the Mean of a Sampled Population

In this scenario the total variance of the data, σ^2, is the sum of two components

$$\sigma^2 = \sigma_M^2 + \sigma_S^2$$

where σ_M^2 is the average analytical method variance (M = "method" or "measurement") and σ_S^2 is the variance of the contaminant concentration in the sampled population (S = "sampling"). The sampling standard deviation σ_S may be affected by the spatial and temporal distribution of the analyte, the extent of the survey unit, the physical sample sizes, and the sample collection procedures. The analytical standard deviation σ_M is affected by laboratory sample preparation, subsampling, and analysis procedures. The value of σ_M may be estimated by the *combined standard uncertainty* of a measured value for a sample whose concentration equals the hypothesized population mean concentration (see Chapter 19, *Measurement Uncertainty*).

The ratio Δ / σ, called the "relative shift," determines the number of samples required to achieve the desired decision error rates α and β. The target value for this ratio should be between 1 and 3, as explained in MARSSIM (2000) and NRC (1998). Ideally, to keep the required number of samples low, one prefers that $\Delta / \sigma \approx 3$. The cost in number of samples rises rapidly as the ratio Δ / σ falls below 1, but there is little benefit from increasing the ratio much above 3.

Generally, it is easier to control σ_M than σ_S. If σ_S is known (approximately), a target value for σ_M can be determined. For example, if $\sigma_S < \Delta / 3$, then a value of σ_M no greater than $\sqrt{\Delta^2 / 9 - \sigma_S^2}$ ensures that $\sigma \le \Delta / 3$, as desired. If $\sigma_S > \Delta / 3$, the requirement that the total σ be less than $\Delta / 3$ cannot be met regardless of σ_M. In the latter case, it is sufficient to make σ_M negligible in comparison to σ_S. Generally, σ_M can be considered negligible if it is no greater than about $\sigma_S / 3$.

Often one needs a method for choosing σ_M in the absence of specific information about σ_S. In this situation, MARLAP recommends the requirement $\sigma_M \le \Delta / 10$ by default. The recommendation is justified below.

Since it is desirable to have $\sigma \le \Delta / 3$, this condition is adopted as a primary requirement. Assume for the moment that σ_S is large. Then σ_M should be made negligible by comparison. As mentioned above, σ_M can be considered negligible if it is no greater than $\sigma_S / 3$. When this condition is met, further reduction of σ_M has little effect on σ and therefore is usually not cost-effective. So, the inequality $\sigma_M \le \sigma_S / 3$ is adopted as a second requirement.

Algebraic manipulation of the equation $\sigma^2 = \sigma_M^2 + \sigma_S^2$ and the required inequality $\sigma_M \le \sigma_S / 3$ gives

$$\sigma_M \le \frac{\sigma}{\sqrt{10}}$$

The inequalities $\sigma \le \Delta / 3$ and $\sigma_M \le \sigma / \sqrt{10}$ together imply the requirement

$$\sigma_M \le \frac{\Delta}{3\sqrt{10}}$$

or approximately

$$\sigma_M \le \frac{\Delta}{10}$$

The required upper bound for the standard deviation σ_M will be denoted by σ_{MR}. MARLAP recommends the equation

$$\sigma_{MR} = \frac{\Delta}{10}$$

by default as a requirement in Scenario I when σ_S is unknown. This upper bound was derived from the assumption that σ_S was large, but it also ensures that the primary requirement $\sigma \le \Delta / 3$ will be met if σ_S is small. When the analytical standard deviation σ_M is less than σ_{MR}, the primary requirement will be met unless the sampling variance, σ_S^2, is so large that σ_M^2 is negligible by comparison, in which case little benefit can be obtained from further reduction of σ_M.

The recommended value of σ_{MR} is based on the assumption that any known bias in the measurement process has been corrected and that any remaining bias is much smaller than the shift, Δ, when a concentration near the gray region is measured. (See Chapter 6, which describes a procedure for testing for bias in the measurement process.)

Achieving an analytical standard deviation σ_M less than the recommended limit, $\Delta / 10$, may be difficult in some situations, particularly when the shift, Δ, is only a fraction of UBGR. When the recommended requirement for σ_M is too costly to meet, project planners may allow σ_{MR} to be larger, especially if σ_S is believed to be small or if it is not costly to analyze the additional samples required because of the larger overall data variance ($\sigma_M^2 + \sigma_S^2$). In this case, project planners may choose σ_{MR} to be as large as $\Delta / 3$ or any calculated value that allows the data quality objectives to be met at an acceptable cost.

The true standard deviation, σ_M, is a theoretical quantity and is never known exactly, but the laboratory may estimate its value using the methods described in Chapter 19, and Section 19.5.13 in particular. The laboratory's estimate of σ_M will be denoted here by u_M and called the "method uncertainty." The method uncertainty, when estimated by uncertainty propagation, is the predicted value of the combined standard uncertainty ("one-sigma" uncertainty) of the analytical

result for a laboratory sample whose concentration equals UBGR. Note that the term "method uncertainty" and the symbol u_M actually apply not only to the method but to the entire measurement process.

In theory, the value σ_{MR} is intended to be an upper bound for the true standard deviation of the measurement process, σ_M, which is unknown. In practice, σ_{MR} is actually used as an upper bound for the method uncertainty, u_M, which may be calculated. Therefore, the value of σ_{MR} will be called the "required method uncertainty" and denoted by u_{MR}. As noted in Chapter 3, MARLAP recommends that project planners specify an MQO for the method uncertainty, expressed in terms of u_{MR}, for each analyte and matrix.

The MQO for method uncertainty is expressed above in terms of the required standard deviation of the measurement process for a laboratory sample whose analyte concentration is at or above UBGR. In principle the same MQO may be expressed as a requirement that the minimum quantifiable concentration (MQC) be less than or equal to UBGR. Chapter 20 defines the MQC as the analyte concentration at which the relative standard deviation of the measured value (i.e., the relative method uncertainty) is $1 / k_Q$, where k_Q is some specified positive value. The value of k_Q in this case should be specified as $k_Q = \text{UBGR} / u_{MR}$. In fact, if the lower bound of the gray region is zero, then one obtains $k_Q = 10$, which is the value most commonly used to define the MQC in other contexts. In practice the requirement for method uncertainty should only be expressed in terms of the MQC when $k_Q = 10$, since to define the MQC with any other value of k_Q may lead to confusion.

EXAMPLE C.1 Suppose the action level is 1 Bq/g and the lower bound of the gray region is 0.6 Bq/g. If decisions are to be made about survey units based on samples, then the required method uncertainty at 1 Bq/g is

$$u_{MR} = \frac{\Delta}{10} = \frac{1\,\text{Bq/g} - 0.6\,\text{Bq/g}}{10} = 0.04\,\text{Bq/g}$$

If this uncertainty cannot be achieved, then an uncertainty as large as $\Delta / 3 = 0.13$ Bq/g may be allowed if σ_S is small or if more samples are taken per survey unit.

EXAMPLE C.2 Again suppose the action level is 1 Bq/g, but this time assume the lower bound of the gray region is 0 Bq/g. In this case the required method uncertainty at 1 Bq/g is

$$u_{MR} = \frac{\Delta}{10} = \frac{1\,\text{Bq/g} - 0\,\text{Bq/g}}{10} = 0.1\,\text{Bq/g}$$

A common practice in the past has been to select an analytical method based on the *minimum detectable concentration* (MDC), which is defined in Chapter 20, *Detection and Quantification Capabilities*. For example, the Multi-Agency Radiation Survey and Site Investigation Manual (MARSSIM, 2000) says:

> During survey design, it is generally considered good practice to select a measure-ment system with an MDC between 10-50% of the DCGL [action level].

Such guidance implicitly recognizes that for cases when the decision to be made concerns the mean of a population that is represented by multiple laboratory samples, criteria based on the MDC may not be sufficient and a somewhat more stringent requirement is needed. It is inter-esting to note that the requirement that the MDC (about 3 times σ_M) be 10 % to 50 % of the action level is tantamount to requiring that σ_M be 0.03 to 0.17 times the action level—in other words, the relative standard deviation should be approximately 10 % at the action level. Thus, the requirement is more naturally expressed in terms of the MQC.

SCENARIO II: Decisions Are to Be Made about Individual Items

In this scenario, the total variance of the data equals the analytical variance, σ_M^2, and the data distribution in most instances should be approximately normal. The decision in this case may be made by comparing the measured concentration, x, plus or minus a multiple of its combined standard uncertainty to the action level. The combined standard uncertainty, $u_c(x)$, is assumed to be an estimate of the true standard deviation of the measurement process as applied to the item being measured; so, the multiplier of $u_c(x)$ equals z_{1-a}, the $(1 - a)$-quantile of the standard normal distribution (see Appendix G, *Statistical Tables*).

Alternatively, if AL = 0, so that any detectable amount of analyte is of concern, the decision may involve comparing x to the critical value of the concentration, x_C, as defined in Chapter 20, *Detection and Quantification Capabilities*.

Case II-1: Suppose the null hypothesis is $X \geq$ AL, so that the action level is the upper bound of the gray region. Given the analytical variance σ_M^2, only a measured result that is less than about UBGR $- z_{1-a}\sigma_M$ will be judged to be clearly less than the action level. Then the desired power of the test $1 - \beta$ is achieved at the lower bound of the gray region only if LBGR $\leq$ UBGR $-$ $z_{1-a}\sigma_M - z_{1-\beta}\sigma_M$. Algebraic manipulation transforms this requirement to

$$\sigma_M \leq \frac{\text{UBGR} - \text{LBGR}}{z_{1-a} + z_{1-\beta}} = \frac{\Delta}{z_{1-a} + z_{1-\beta}}$$

Case II-2: Suppose the null hypothesis is $X \leq$ AL, so that the action level is the lower bound of the gray region. In this case, only a measured result that is greater than about LBGR $+ z_{1-a}\sigma_M$

will be judged to be clearly greater than the action level. The desired power of the test $1 - \beta$ is achieved at the upper bound of the gray region only if $\text{UBGR} \geq \text{LBGR} + z_{1-\alpha}\sigma_M + z_{1-\beta}\sigma_M$. Algebraic manipulation transforms this requirement to

$$\sigma_M \leq \frac{\text{UBGR} - \text{LBGR}}{z_{1-\alpha} + z_{1-\beta}} = \frac{\Delta}{z_{1-\alpha} + z_{1-\beta}}$$

So, in either case, the requirement remains that:

$$\sigma_M \leq \frac{\Delta}{z_{1-\alpha} + z_{1-\beta}}$$

Therefore, MARLAP recommends the use of the equation

$$u_{MR} = \sigma_{MR} = \frac{\Delta}{z_{1-\alpha} + z_{1-\beta}}$$

as an MQO for method uncertainty when decisions are to be made about individual items (i.e., laboratory samples) and not about population parameters.

If both α and β are at least 0.05, one may use the value $u_{MR} = 0.3\Delta$.

The recommended value of u_{MR} is based on the assumption that any known bias in the measurement process has been corrected and that any remaining bias is small relative to the method uncertainty.

If LBGR = 0, then Δ = UBGR and $\sigma_{MR} = \Delta / (z_{1-\alpha} + z_{1-\beta})$ implies

$$\sigma_M \leq \frac{\text{UBGR}}{z_{1-\alpha} + z_{1-\beta}}$$

This requirement is essentially equivalent to requiring that the MDC not exceed UBGR. Thus, when LBGR = 0, the MQO may be expressed in terms of the detection capability of the analytical method.

Note that when AL = LBGR = 0, the MQO for detection capability may be derived directly in terms of the MDC, since the MDC is defined as the analyte concentration at which the probability of detection is $1 - \beta$ when the detection criterion is such that the probability of false detection in a sample with zero analyte concentration is at most α.

EXAMPLE C.3 Suppose the action level is $1\ \text{Bq/L}$, the lower bound of the gray region is 0.5 Bq/L, $\alpha = 0.05$, and $\beta = 0.10$. If decisions are to be made about individual items, then the required method uncertainty at $1\ \text{Bq/L}$ is

$$u_{MR} = \frac{\Delta}{z_{1-\alpha} + z_{1-\beta}} = \frac{1\ \text{Bq/L} - 0.5\ \text{Bq/L}}{z_{0.95} + z_{0.90}} = \frac{0.5\ \text{Bq/L}}{1.645 + 1.282} = 0.17\ \text{Bq/L}.$$

## C.4 The Role of the MQO for Method Uncertainty in Data Evaluation

This section provides guidance and equations for determining warning and control limits for QC sample results based on the project-specific MQO for method uncertainty. In the MARLAP Process as described in Chapter 1, these warning and control limits are used in the ongoing evaluation of protocol performance (see Chapter 7, *Evaluating Methods and Laboratories*) and in the evaluation of the laboratory data (see Chapter 8, *Radiochemical Data Verification and Validation*).

C.4.1 Uncertainty Requirements at Various Concentrations

When project planners follow MARLAP's recommendations for establishing MQOs for method uncertainty for method selection and development, the maximum allowable standard deviation, σ_{MR}, at the upper bound of the gray region is specified. During subsequent data evaluation, the standard deviation at any concentration less than UBGR should be at most σ_{MR}, and the relative standard deviation at any concentration greater than UBGR should be at most σ_{MR}/UBGR, which will be denoted here by φ_{MR}. Note that, since the true standard deviation can never be known exactly, in practice the requirement is expressed in terms of the required method uncertainty, u_{MR}, to which the combined standard uncertainty of each result may be compared.

EXAMPLE C.4 Consider the preceding example, in which AL = UBGR = $1\ \text{Bq/L}$, LBGR = $0.5\ \text{Bq/L}$, and $u_{MR} = 0.17\ \text{Bq/L}$. In this case the combined standard uncertainty for any measured result, x, should be at most $0.17\ \text{Bq/L}$ if $x < 1\ \text{Bq/L}$, and the relative combined standard uncertainty should be at most $0.17 / 1$, or $17\ \%$, if $x > 1\ \text{Bq/L}$.

In Scenario I, where decisions are made about the mean of a population based on multiple physical samples (e.g., from a survey unit), if the default value $u_{MR} = \Delta / 10$ is assumed for the required method uncertainty, then the required bound for the analytical standard deviation as a function of concentration is as shown in Figure C.1. The figure shows that the bound, u_{Req}, is constant at all concentrations, x, below UBGR, and u_{Req} increases with x when x is above UBGR. So, $u_{Req} = u_{MR}$ when $x <$ UBGR and $u_{Req} = x \cdot u_{MR}/\text{UBGR}$ when $x >$ UBGR.
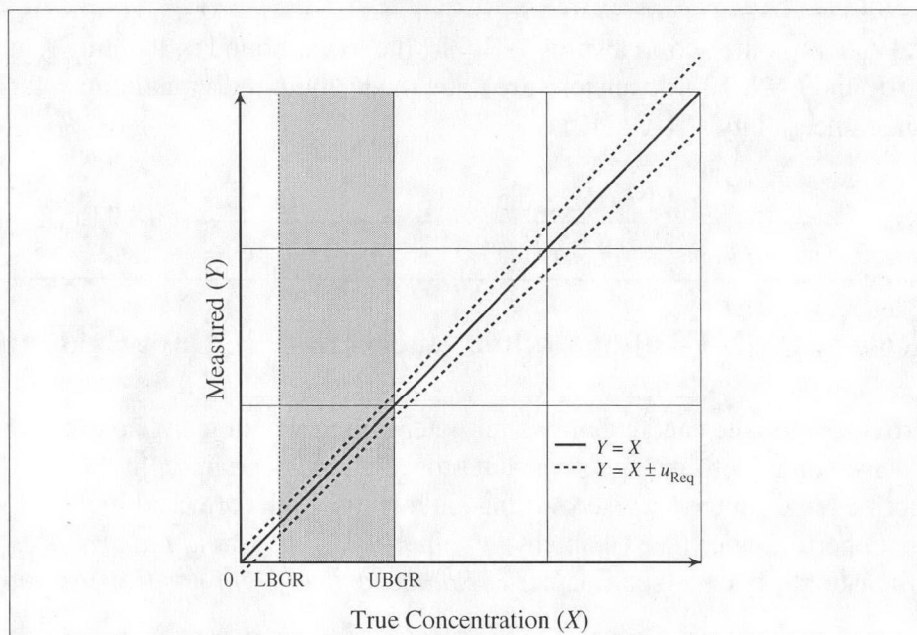
FIGURE C.1 — Required analytical standard deviation (u_{Req})

These requirements can be relaxed somewhat for samples with very high analyte concentrations as long as the project's requirements for decision uncertainty are met. However, MARLAP does not provide specific guidance to address this issue for Scenario I.

In Scenario II, where decisions are made about individual physical samples, it is possible to widen the required bounds for the standard deviation at any concentration outside the gray region. For example, suppose UBGR = AL, LBGR is set at some concentration below UBGR, and the decision error probabilities α and β are specified. Then the project planners require the probability of a Type I error not to exceed α when the true concentration is at or above UBGR, and they require the probability of a Type II error not to exceed β when the true concentration is at or below LBGR. The decision rule is based on the combined standard uncertainty of the measurement result: any sample whose measured concentration, x, exceeds AL minus $z_{1-\alpha}$ times the combined standard uncertainty, $u_c(x)$, is assumed to exceed the action level. So, assuming $u_c(x)$ is an adequate estimate of the analytical standard deviation, the planners' objectives are met if

$$
u_c(x) \leq
\begin{cases}
\dfrac{\text{UBGR} - x}{z_{1-\alpha} + z_{1-\beta}}, & \text{if } x \leq \text{LBGR} \\[2em]
\dfrac{x - \text{LBGR}}{z_{1-\alpha} + z_{1-\beta}}, & \text{if } x \geq \text{UBGR} \\[2em]
\dfrac{\Delta}{z_{1-\alpha} + z_{1-\beta}}, & \text{if } \text{LBGR} \leq x \leq \text{UBGR}
\end{cases}
$$

EXAMPLE C.5 Consider the earlier example in which AL = UBGR = 1.0 Bq/L, LBGR = 0.5 Bq/L, α = 0.05, β = 0.10, and u_{MR} = 0.17 Bq/L. The less restrictive uncertainty requirement can be expressed as

$$u_c(x) \leq \begin{cases} \dfrac{1.0\,\text{Bq/L} - x}{2.927}, & \text{if } x \leq 0.5\,\text{Bq/L} \\[2mm] \dfrac{x - 0.5\,\text{Bq/L}}{2.927}, & \text{if } x \geq 1.0\,\text{Bq/L} \\[2mm] 0.17, & \text{if } 0.5\,\text{Bq/L} \leq x \leq 1.0\,\text{Bq/L} \end{cases}$$

So, if x = 0, the requirement is $u_c(x) \leq$ (1 Bq/L) / 2.927 = 0.34 Bq/L, and, if x = 2 Bq/L, the requirement is $u_c(x) \leq$ (2 Bq/L - 0.5 Bq/L) / 2.927 = 0.51 Bq/L, which is approximately 26 % in relative terms.

C.4.2 Acceptance Criteria for Quality Control Samples

The next issue to be addressed is how to set warning and control limits for quality control (QC) sample results. These limits will be used by project data assessors to determine whether the laboratory appears to be meeting MQOs. Presumably the lab has stricter internal QC requirements (see Chapter 18, *Laboratory Quality Control*).

The development of acceptance criteria for QC samples will be illustrated with an example. Assume UBGR = 5 Bq/g (soil) and LBGR = 1.5 Bq/g. The width of the gray region is Δ = 5 - 1.5 = 3.5 Bq/g. Project planners, following MARLAP's guidance, choose the required method uncertainty at 5 Bq/g (UBGR) to be

$$u_{MR} = \frac{\Delta}{10} = 0.35\,\text{Bq/g}$$

or 7 %. So, the maximum standard uncertainty at analyte concentrations less than 5 Bq/g should be u_{MR} = 0.35 Bq/g, and the maximum *relative* standard uncertainty at concentrations greater than 5 Bq/g should be φ_{MR} = 0.07, or 7 %.

Although it is possible to relax these uncertainty criteria for samples with very high analyte concentrations, MARLAP recommends that the original criteria be used to develop acceptance limits for the results of QC sample analyses.

C.4.2.1 Laboratory Control Samples

It is assumed that the concentration of a laboratory control sample (LCS) is high enough that the relative uncertainty limit $\varphi_{MR} = 0.07$ is appropriate. The *percent deviation* for the LCS analysis is defined as

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

where

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

It is assumed that the uncertainty of SA is negligible; so, the maximum allowable relative standard deviation of $\%D$ is the same as that of the measured result itself, or $\varphi_{MR} \times 100 \%$. Then the 2-sigma warning limits for $\%D$ are $\pm 2\varphi_{MR} \times 100 \%$ and the 3-sigma control limits are $\pm 3\varphi_{MR} \times 100 \%$. (In situations where φ_{MR} is very small, the uncertainty of SA should not be ignored.)

The requirements for LCSs are summarized below.

Laboratory Control Samples	
Statistic:	$\%D = \dfrac{SSR - SA}{SA} \times 100 \%$
Warning limits:	$\pm 2\varphi_{MR} \times 100 \%$
Control limits:	$\pm 3\varphi_{MR} \times 100 \%$

EXAMPLE C.6

(UBGR $= 5$ Bq/g, $u_{MR} = 0.35$ Bq/g, $\varphi_{MR} = 0.07$.)

Suppose an LCS is prepared with a concentration of SA $= 10$ Bq/g and the result of the analysis is 11.61 Bq/g with a combined standard uncertainty of 0.75 Bq/g. Then

$$\%D = \frac{11.61 \text{ Bq/g} - 10 \text{ Bq/g}}{10 \text{ Bq/g}} \times 100 \% = 16.1 \%$$

The warning limits in this case are

$$\pm 2\varphi_{MR} \times 100\,\% = \pm 14\,\%$$

and the control limits are

$$\pm 3\varphi_{MR} \times 100\,\% = \pm 21\,\%$$

So, the calculated value of %D is above the upper warning limit but below the control limit.

C.4.2.2 Duplicate Analyses

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

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

When $\bar{x} <$ UBGR, the warning limit for the absolute difference $|x_1 - x_2|$ is

$$2u_{MR}\sqrt{2} \approx 2.83\,u_{MR}$$

and the control limit is

$$3u_{MR}\sqrt{2} \approx 4.24\,u_{MR}$$

Only upper limits are used, because the absolute value $|x_1 - x_2|$ is being tested.

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

$$RPD = \frac{|x_1 - x_2|}{\bar{x}} \times 100\,\%$$

The warning limit for RPD is

$$2\varphi_{MR}\sqrt{2} \times 100\,\% \approx 2.83\,\varphi_{MR} \times 100\,\%$$

and the control limit is

$$3\varphi_{MR}\sqrt{2} \times 100\,\% \approx 4.24\,\varphi_{MR} \times 100\,\%$$

The requirements for duplicate analyses are summarized below.

Duplicate Analyses

If $\bar{x}$ < UBGR:

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

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

Statistic: $\qquad$ $RPD = \dfrac{|x_1 - x_2|}{\bar{x}} \times 100\ \%$

Warning limit: $\qquad$ $2.83\ \varphi_{MR} \times 100\ \%$

Control limit: $\qquad$ $4.24\ \varphi_{MR} \times 100\ \%$

EXAMPLE C.7

(UBGR = 5 Bq/g, $u_{MR} = 0.35$ Bq/g, $\varphi_{MR} = 0.07$)

Suppose duplicate analyses are performed on a laboratory sample and the results of the two measurements are

$x_1 = 9.0$ Bq/g with combined standard uncertainty $u_c(x_1) = 2.0$ Bq/g
$x_2 = 13.2$ Bq/g with combined standard uncertainty $u_c(x_2) = 2.1$ Bq/g

The duplicate results are evaluated as follows.

$$\bar{x} = \frac{9.0\,\text{Bq/g} + 13.2\,\text{Bq/g}}{2} = 11.1\ \text{Bq/g}$$

Since $\bar{x} \geq 5$ Bq/g, the acceptance criteria are expressed in terms of RPD.

$$RPD = \frac{|9.0\,\text{Bq/g} - 13.2\,\text{Bq/g}|}{11.1\,\text{Bq/g}} \times 100\ \% = 37.84\ \%$$

The warning and control limits for RPD are

Warning limit = $2.83 \times 0.07 \times 100\ \% = 19.81\ \%$
Control limit = $4.24 \times 0.07 \times 100\ \% = 29.68\ \%$

In this case, the value of RPD is above the control limit. (Also note that the relative standard uncertainties are larger than the 7 % required for concentrations above 5 Bq/g.)

C.4.2.3 Method Blanks

Case 1. If an aliquant of blank material is analyzed, or if a nominal aliquant size is used in the data reduction, the measured blank result is an activity concentration. The target value is zero, but the measured value may be either positive or negative. So, the 2-sigma warning limits are $\pm 2u_{MR}$ and the 3-sigma control limits are $\pm 3u_{MR}$.

Case 2. If no blank material is involved (only reagents, tracers, etc., are used), the measured result may be a total activity, not a concentration. In this case the method uncertainty limit u_{MR} should be multiplied by the nominal or typical aliquant size, m_S. Then the 2-sigma warning limits are $\pm 2u_{MR}m_S$ and the 3-sigma control limits are $\pm 3u_{MR}m_S$.

The requirements for method blanks are summarized below.

Method Blanks

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

Total Activity:
Statistic:	Measured total activity
Warning limits:	$\pm 2u_{MR}m_S$
Control limits:	$\pm 3u_{MR}m_S$

EXAMPLE C.8

(UBGR = 5 Bq/g, u_{MR} = 0.35 Bq/g, φ_{MR} = 0.07)

Suppose a method blank is analyzed and the result of the measurement is

x = 0.00020 Bq with combined standard uncertainty $u_c(x)$ = 0.00010 Bq

Assuming the nominal aliquant mass is 1.0 g, or m_S = 0.001 g, the result is evaluated by comparing x to the warning and control limits:

$$\pm 2u_{MR}m_S = \pm 0.00070 \text{ Bq}$$
$$\pm 3u_{MR}m_S = \pm 0.00105 \text{ Bq}$$

In this case x is within the warning limits.

C.4.2.4 Matrix Spikes

The acceptance criteria for matrix spikes are more complicated than those described above for laboratory control samples because of pre-existing activity in the unspiked sample, which must be measured and subtracted from the activity measured after spiking. The *percent deviation* for a matrix spike is defined as

$$\%D = \frac{SSR - SR - SA}{SA} \times 100 \ \%$$

where
> SSR is the spiked sample result
> SR is the unspiked sample result
> SA is the spike concentration added (total activity divided by aliquant size).

However, warning and control limits for $\%D$ depend on the measured values; so, $\%D$ is not a good statistic to use for matrix spikes. A better statistic is the "Z score":

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

where "$\max(x, y)$" denotes the maximum of x and y. Then warning and control limits for Z are set at ± 2 and ± 3, respectively. (It is assumed again that the uncertainty of SA is negligible.) The requirements for matrix spikes are summarized below.

Matrix Spikes

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

Warning limits: ± 2
Control limits: ± 3

EXAMPLE C.9

($UBGR = 5 \ Bq/g$, $u_{MR} = 0.35 \ Bq/g$, $\varphi_{MR} = 0.07$)

Suppose a matrix spike is analyzed. The result of the original (unspiked) analysis is

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SR = 3.5 Bq/g with combined standard uncertainty $u_c(SR) = 0.29$ Bq/g

the spike concentration added is

SA = 10.1 Bq/g with combined standard uncertainty $u_c(SA) = 0.31$ Bq/g

and the result of the analysis of the spiked sample is

SSR = 11.2 Bq/g with combined standard uncertainty $u_c(SSR) = 0.55$ Bq/g

Since SR is less than UBGR (5), max(SR, UBGR) = UBGR = 5. So,

$$Z = \frac{\text{SSR} - \text{SR} - \text{SA}}{\varphi_{MR}\sqrt{\text{SSR}^2 + \text{UBGR}^2}} = \frac{11.2\,\text{Bq/g} - 3.5\,\text{Bq/g} - 10.1\,\text{Bq/g}}{0.07\sqrt{(11.2\,\text{Bq/g})^2 + (5\,\text{Bq/g})^2}} = -2.80$$

So, Z is less than the lower warning limit (–2) but slightly greater than the lower control limit (–3).

C.5 References

U.S. Environmental Protection Agency (EPA). 2000. *Guidance for the Data Quality Objectives (DQO) Process*. EPA QA/G-4. EPA/600/R-96/055. Office of Environmental Information, Washington, DC. Available at www.epa.gov/quality/qa_docs.html.

MARSSIM. 2000. *Multi-agency Radiation Survey and Site Investigation Manual* (MARSSIM) Rev. 1. NUREG-1575, Nuclear Regulatory Commission, Washington, DC. EPA 402-R-97-016, Environmental Protection Agency, Washington, DC. Available from www.epa.gov/radiation/marssim/.

Nuclear Regulatory Commission (NRC). 1998. *A Nonparametric Statistical Methodology for the Design and Analysis of Final Status Decommissioning Surveys*. NUREG-1505. NRC, Washington, DC.

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-

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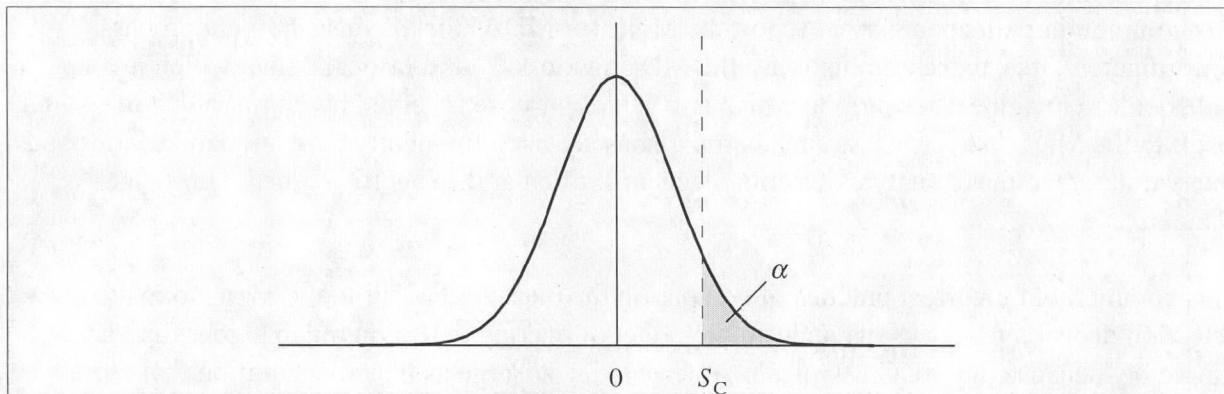
FIGURE 3B.1 — The critical value of the net signal

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.

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[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.

Analytical Protocol Specifications

Analyte List: ^{90}Sr

Matrix: Raw Milk

Concentration Range: 1 to 50 pCi/L

Method Validation Level: MARLAP Levels A, C, or D as applicable. See Attachment C for details.

MQOs: A method uncertainty (u_{MR}) of 0.5 pCi/L at 8 pCi/L

Analysis Limitations: Perform direct measurement of analyte. Analysis of progeny allowed if radioactive equilibrium is established at laboratory from freshly isolated parent.

Possible Interferences: Fresh beta-emitting, fission-product nuclides if purification steps are inadequate or non-existent.

Action Level: 8 pCi/L

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	Sample size > 3.5 L; Preserve on ice or with 5 mL of 37% formaldehyde / L sample
Sample Receipt and Inspection	Return sample receipt acknowledgment letter with date of receipt at Lab. Cross index list for Sample ID and assigned Lab ID. Visually inspect containers upon receipt to ensure integrity and normal sample appearance. Rad survey samples upon receipt. COC documentation applies.
Laboratory Sample Preparation	Take sufficient aliquant of sample after gamma-ray spectrometry analysis (see separate requirements in the gamma spectroscopy APS). Keep 1 liter as backup until analytical results have been approved by project manager.
Sample Dissolution	None
Chemical Separations	Isolation of Sr from the milk by either cation resin or precipitation of Sr from soured or dry-ashed milk. Separation from Ca is essential. Rare earth and Ba scavenging steps are necessary to eliminate possible interferences from fresh fission products.
Preparing Sources for Counting	Final source mount to accommodate nuclear instrumentation.
Nuclear Counting	Acceptable counting instrumentation includes: Liquid Scintillation Counter, Gas Proportional Counter or Solid State Beta Detector. Detection method to discriminate to the extent possible for potential ^{89}Sr contamination by physical or calculations means.
Data Reduction and Reporting	See Attachment A
Sample Tracking Requirements	Chain-of-Custody
Other - Chemical Yielding	Gravimetric (must have 99% Ca removal) or ^{85}Sr tracer with > 90% Ca removal.

* Spiking range provided in Attachment B

April 25, 2005

Attachment A
Data Reduction and Reporting Requirements

Data Reduction

1. Calculation of Sr-90 activity or concentration (pCi/L) can be based on the quantification of Sr-90 and/or Y-90, with proper addressing of decay and ingrowth of Y-90.
2. Calculation of the associated combined standard uncertainty (pCi/L) of the ^{90}Sr concentration.
3. Calculation of the MDC, in terms of pCi/L, shall be sample specific using the detector efficiency and background, counting time, decay and ingrowth factors, Sr yield and sample volume used for the analysis.
4. Calculation of critical level, in terms of pCi/L, shall be sample specific.
5. Calculation of gross, net and background count rate, detector efficiency, chemical yield, decay and ingrowth factors for each sample.
6. Initial review and approval of data reduction equations shall be established during a desk or onsite audit as part of the lab approval/contracting process.
7. No changes in the equations used in data reduction shall be initiated without prior approval of the project manager.

Data Reporting

1. For each sample, the following sample specific parameters shall be reported:
   Batch #, Sample ID, Lab ID, sample collection (reference) date, sample receipt date, estimated (or actual) sample volume received, ^{90}Y separation date, counting date, cross reference to batch QC samples, SOP used, analyst, data reviewer and report date.
2. For each sample, the following sample processing parameters or factors shall be reported:
   Gross, net and background count rates, detector efficiency, sample volume processed, ^{90}Sr decay factor, ^{90}Y decay and ingrowth factors (and times), and chemical yield factor.
3. For each sample the following calculated information will be reported:
   critical level, MDC, ^{90}Sr concentration and associated combined standard uncertainty (CSU).
4. Batch quality control results for the laboratory control sample (LCS), method blank, duplicate sample and matrix spike sample shall be reported with each batch of samples:
   Reporting data to include:
   LCS - calculated sample and prepared spike concentration with associated CSUs, and percent difference between sample result and known value
   Duplicate samples - calculated concentrations with associated CSU for both samples
   Matrix spike - calculated sample and known spike concentration with associated CSUs, and percent difference between sample results
5. A "Narrative" shall be provided with each batch of samples that describes problems encountered or noted discrepancies for any sample, possible effect on the quality of a result and actions taken to remedy the problem if recurrent.
6. Reports shall be provided electronically and as a hard copy. An electronic data format will be provided.

Attachment B
Batch Quality Control Sample Evaluation Criteria

A "batch" of samples is defined as 20 samples or less including the QC samples. The results of the batch QC samples shall be evaluated according to the equations provided below. It should be noted that no action is to be taken when a "not to exceed" limit stated below is exceeded for an individual sample. However, if trending of the results indicate many results or a trend of results exceeds a limit, actions must be taken to stop processing samples, identify the root cause of the problem and take corrective actions. Sample processing can resume when the corrective actions have been shown to be effective in eliminating the cause of the problem. It is expected that the Laboratory's QA officer and project manager shall provide oversight on the sample processing and shall track the batch QC results.

Laboratory Control Sample

The ^{90}Sr spike concentration of an LCS shall be between 10 and 20 pCi/L and the spiking uncertainty should be $\leq 5\%$. The percent deviation (%D) for the LCS analysis is defined as

$$\%D \doteq \frac{SSR - SA}{SA} \times 100\% \qquad \qquad 1)$$

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

The %D control limit is $\pm 3\ \varphi_{MR} \times 100\%$ or $\pm 19\%$. For long-term trending, the %D results should be plotted graphically in terms of a quality control chart with the expected mean %D value of zero.

Duplicate Samples

The acceptance criterion for duplicate analysis results depends on the analyte concentration of the sample, which is determined by the average $\bar{x}$ of the two measured results x_1 and x_2.

$$\bar{x} = \frac{x_1 + x_2}{2} \qquad \qquad 2)$$

When $\bar{x} < 8$, the control limit for the absolute difference $|x_1 - x_2|$ is 4.24 u_{MR} or 2.1.

When $\bar{x} \geq 8$ pCi/L, the control limit for the *relative percent difference* (RPD), defined as,

$$RPD = \frac{|x_1 - x_2|}{\bar{x}} \times 100\% \qquad \qquad 3)$$

is 4.24 $\varphi_{MR} \times 100\%$ or 27 %. For long-term trending, the absolute difference and RPD results should be plotted graphically in terms of a quality control chart with an expected absolute difference and RPD mean values of zero.

Matrix Spikes

The acceptance criteria for matrix spikes uses the "Z score," defined below, as the test for matrix spikes. The pre-existing activity (or concentration) must be measured and subtracted from the activity measured after spiking. The ^{90}Sr spike concentration of a matrix spike shall be between 10 and 20 pCi/L and the spiking uncertainty should be $\leq 5\%$.

$$Z = \frac{SSR - SR - SA}{\varphi_{MR}\sqrt{SSR^2 + max(SR, UBGR)^2}}$$ (4)

$$Z = \frac{SSR - SR - SA}{0.0625\sqrt{SSR^2 + max(SR, 8)^2}}$$ (5)

where:
- SSR   is the spiked sample result,
- SR   is the unspiked sample result,
- SA   is the spike concentration added (total activity divided by aliquant mass), and max(SR,8) denotes the maximum of SR and 8 pCi/L.

The control limit for Z is set at ± 3. It is assumed that the uncertainty of SA is negligible with respect to the uncertainty of SSR. For long-term trending, the Z results should be plotted graphically in terms of a quality control chart with a Z value of zero as the expected mean value.

Method Blanks When an aliquant of a blank material is analyzed, the target value is zero. However, the measured value may be either positive or negative. The applicable control limit for blank samples shall be within $\pm 3\ u_{MR}$ or ± 1.5 pCi/L. For long-term trending, the blank results should be plotted graphically in terms of a quality control chart with an expected mean value of zero.

Prior to processing any milk samples, the laboratory is required to validate its ^{90}Sr in milk radioanalytical method according to the specifications stated in MARLAP Chapter 6. The level of method validation will depend on whether the laboratory has a previously validated method for ^{90}Sr in milk (Level A), will modify a previously validated ^{90}Sr method for a milk matrix (Level C) or must newly develop or adapt a method for ^{90}Sr in milk (Level D). The laboratory shall submit the method validation documentation to the project manager for review and approval prior to the acquisition of a laboratory contract. A summary of the method validation criteria is presented below for the three validation levels.

Level A method validation pertains to a previously validated method for ^{90}Sr in milk. No additional testing is required if the method previously has been successfully validated and the available method validation documentation has been reviewed and approved by the project manager. Documentation of method validation should conform to the specifications provided below.

Level C method validation is to be conducted when a validated ^{90}Sr method for a non-milk matrix is modified for applicability for the milk matrix, e.g., when the EPA 905 ^{90}Sr in water method is modified for use with a milk matrix. A method validation plan should be developed and documented. Validation Level C requires the preparation and analysis of five replicate milk samples (internal performance testing samples) spiked at three different concentrations. For this project the three levels of 1, 10, 20 pCi/L (or within ± 15% of the values) should be used in the validation process. Each sample result for the lowest level (below the action level) must be within ± 2.9 u_{MR} or ± 1.45 pCi/L of the spiked concentration value. Each sample result from the two higher spiked levels (above the action level) must be within ± 2.9 φ_{MR} × 100% or ± 18% of the spiked concentration value. Documentation of method validation should conform to the specifications provided below.

Level D method validation is to be conducted when a new method is specifically developed or adapted from the literature for the project's ^{90}Sr in milk application. Validation Level D requires the preparation and analysis of seven replicate milk samples (internal performance testing samples) spiked at three different concentrations. For this project the three levels of 1, 10, 20 pCi/L (or within ± 15% of the values) should be used in the validation process. Each sample result for the lowest level (below the action level) must be within ± 3.0 u_{MR} or ± 1.5 pCi/L of the spiked concentration value. Each sample result from the two higher spiked levels (above the action level) must be within ± 3.0 φ_{MR} × 100% or ± 19% of the spiked concentration value. Documentation of method validation should conform to the specifications provided below.

Method Validation Documentation

Documentation to be submitted to the project manager includes: Method Validation Plan, Method Number, Analyst(s) analyzing the samples, spiked concentration values, experimental results and comparison to the acceptable performance criteria for the validation level.

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RADIOACTIVITY SOLUTIONS

Data Report for: XYZ Nuclear Handlers, Incorporated
Sample Matrix: Whole Milk

QUALITY CONTROL GRAPHS
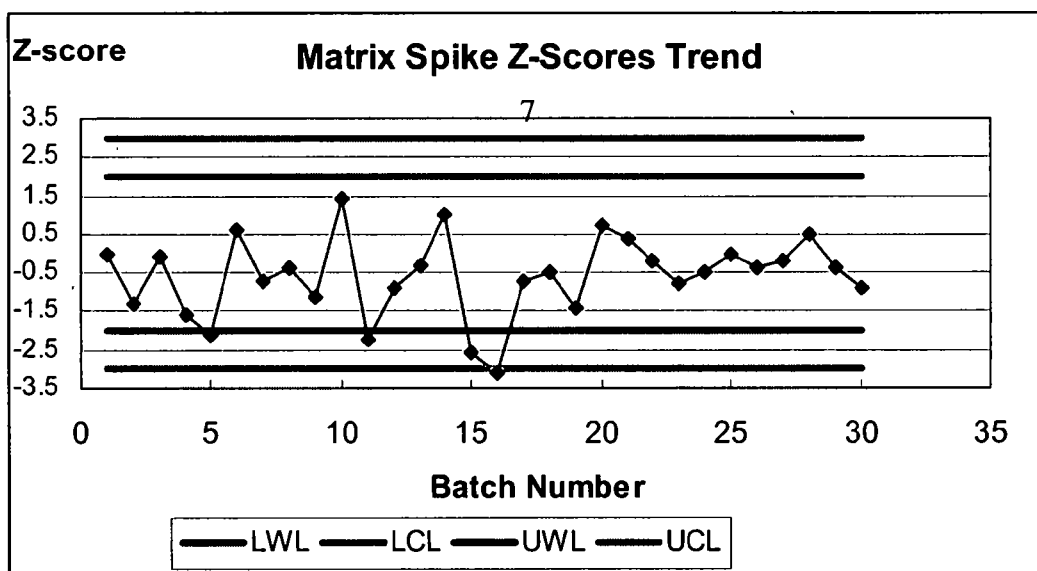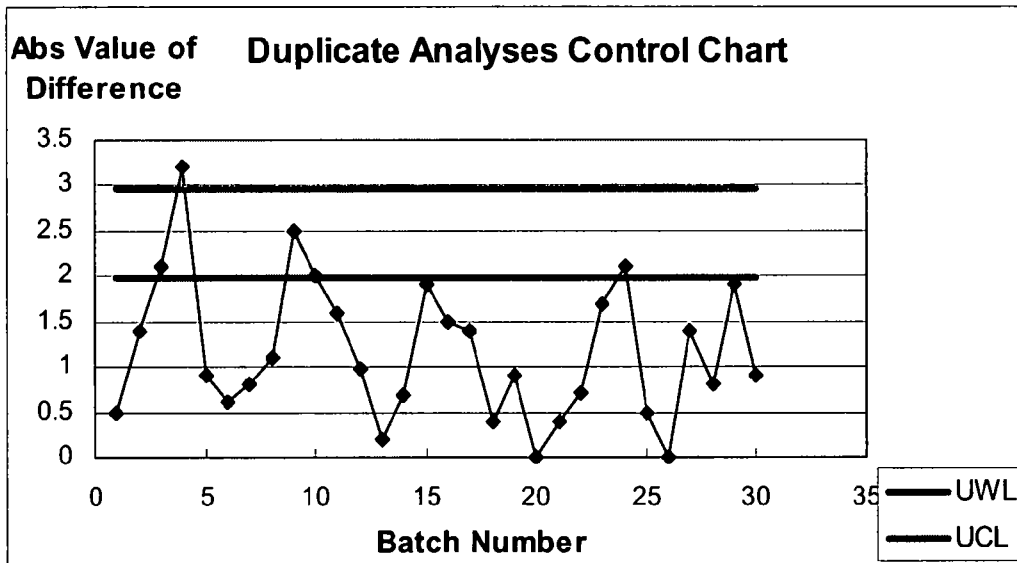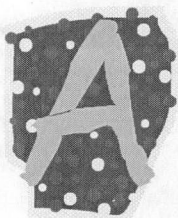
LCS QC Chart for Sr-90

pCi/L

Batch Number

LWL ——— LCL ——— UWL ——— UCL

Blank Results Sr-90 in Milk

pCi/L

Batch

LWL ——— LCL ——— UWL ——— UCL

Duplicate Analyses Control Chart

Matrix Spike Z-Scores Trend

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RADIOACTIVITY SOLUTIONS

Data Report for: XYZ Nuclear Handlers, Incorporated
Sample Matrix: Whole Milk
Date Samples Received: April 18, 2006

Sample Name – Lab ID	Sample Date	Analysis Start Time	Analysis Completed	Analyte	Activity ± 1σ, pCi/L	MDC, pCi/L
Guernsey 1 051002	3/24/05	4/4/05	4/11/05	^{90}Sr	1.61 ± 0.38	0.80
Jersey 5 051003	3/24/05	4/4/05	4/07/05	^{90}Sr	0.52 ± 0.36	1.2
Holstein 3 051004	3/24/05	4/4/05	4/11/05	^{90}Sr	1.10 ± 0.37	0.68
Guernsey 6 051005	3/24/05	4/4/05	4/11/05	^{90}Sr	-0.55 ± 0.93	0.50
Jersey 8 051006	3/25/05	4/4/05	4/11/05	^{90}Sr	1.55 ± 0.37	0.61
Guernsey 1 DU 051008	4/4/05	4/4/05	4/11/05	^{90}Sr	1.95 ± 0.38	0.85
Batch Blank 051009	4/4/05	4/4/05	4/11/05	^{90}Sr	-0.43 ± 0.66	1.3
LCS 051007	4/4/05	4/4/05	4/11/05	^{90}Sr	12.81 ± 0.49	1.5
Jersey 8 MS 051010	4/4/05	4/4/05	4/11/05	^{90}Sr	15.50 ± 0.51	1.6

Matrix Spike: 20.0 pCi/L added.
LCS Target: 10.0 pCi/L
Analysis by Liquid Scintillation Counting
Critical Level ~ 0.6 pCi/L

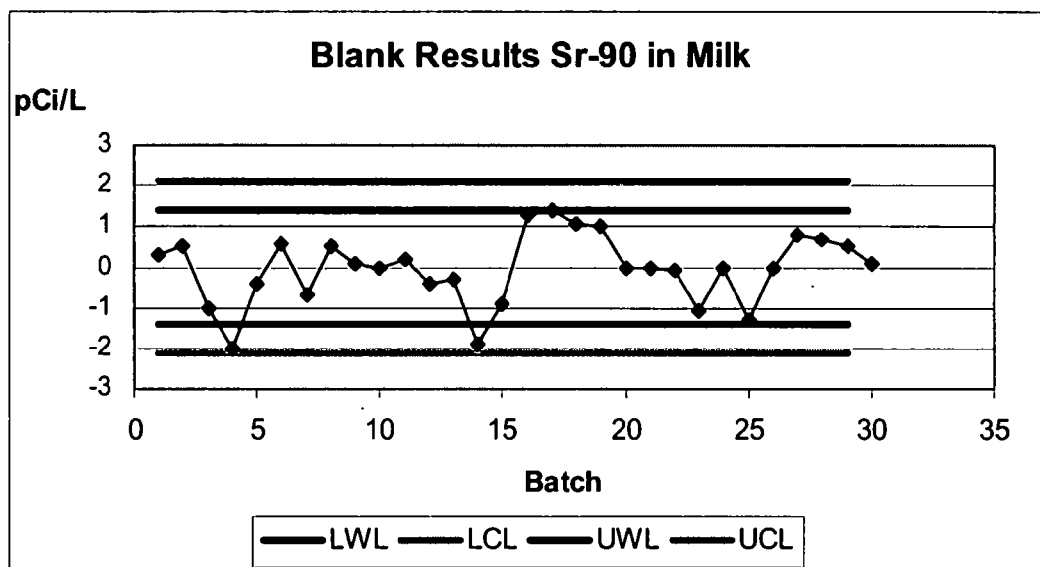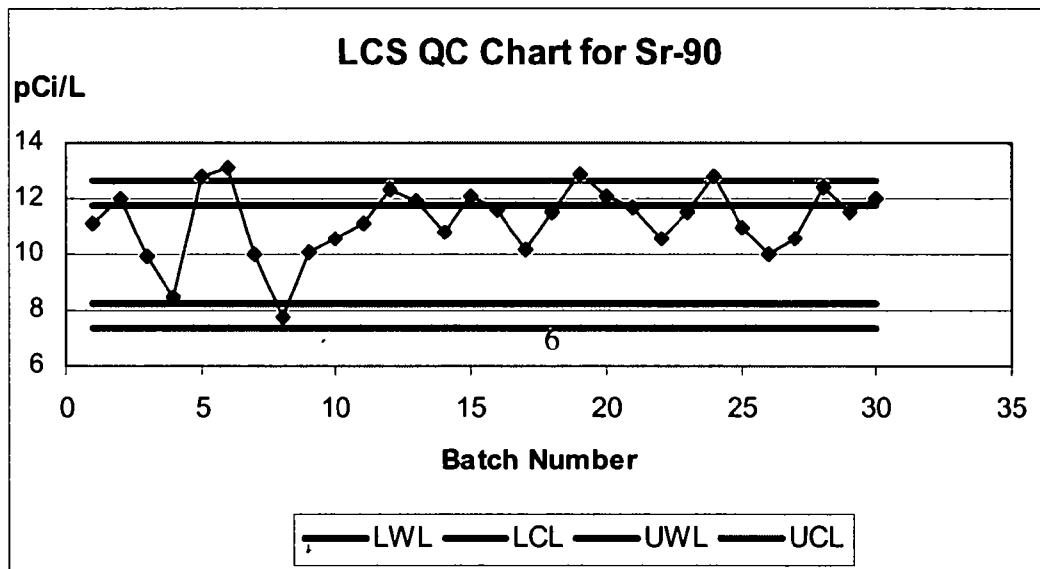Approved by: I. M. Wright, QA Officer

A PLUS

RADIOACTIVITY SOLUTIONS

Data Report for: XYZ Nuclear Handlers, Incorporated
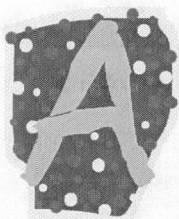Sample Matrix: Whole Milk
Date Samples Received: April 18, 2006

Sample Name – Lab ID	Sample Date	Analysis Start Time	Analysis Completed	Analyte	Activity ± 1σ, pCi/L	MDC, pCi/L	Initial Data Qualifiers Based on Sample Results
Guernsey 1 051002	3/24/05	4/4/05	4/11/05	^{90}Sr	1.61 ± 0.38	0.80	
Jersey 5 051003	3/24/05	4/4/05	4/07/05	^{90}Sr	0.52 ± 0.36	1.2	U, E*
Holstein 3 051004	3/24/05	4/4/05	4/11/05	^{90}Sr	1.10 ± 0.37	0.68	
Guernsey 6 051005	3/24/05	4/4/05	4/11/05	^{90}Sr	-0.55 ± 0.93	0.50	U
Jersey 8 051006	3/25/05	4/4/05	4/11/05	^{90}Sr	1.55 ± 0.37	0.61	
							QC Test Qualifiers
Guernsey 1 DU 051008	4/4/05	4/4/05	4/11/05	^{90}Sr	1.95 ± 0.38	0.85	
Batch Blank 051009	4/4/05	4/4/05	4/11/05	^{90}Sr	-0.43 ± 0.66	1.3	E, Q*
LCS 051007	4/4/05	4/4/05	4/11/05	^{90}Sr	12.81 ± 0.49	1.5	S(+), E*
Jersey 8 MS 051010	4/4/05	4/4/05	4/11/05	^{90}Sr	15.50 ± 0.51	1.6	S(-), E*

Matrix Spike: 20.0 pCi/L added.
LCS Target: 10.0 pCi/L
Analysis by Liquid Scintillation Counting
Critical Level ~ 0.6 pCi/L

out of control, but trivial

Approved by: <u>I. M. Wright, QA Officer</u>

*The grayed-out qualifiers in the final column (E, Q) are present only as part of this exercise. These qualifiers generally would NOT be applied to the QC samples. This is particularly true for the matrix spike and the LCS where the MDC is relatively unimportant when the measured concentraiton is obviously real. The E that was added in the sample section indicates that the MDC required in the APS of 1.0 pCi/L was not met. In this case, the E may or may not be retained by the data validator.

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Data Report for: XYZ Nuclear Handlers, Incorporated
Sample Matrix: Whole Milk
Date Samples Received: April 18, 2006

Sample Name – Lab ID	Sample Date	Analysis Start Time	Analysis Completed	Analyte	Activity ± 1σ, pCi/L	MDC, pCi/L	All Qualifiers
Guernsey 1 051002	3/24/05	4/4/05	4/11/05	^{90}Sr	1.61 ± 0.38	0.80	**S(+,-)**
Jersey 5 051003	3/24/05	4/4/05	4/07/05	^{90}Sr	0.52 ± 0.36	1.2	**S(+,-), U,** E*
Holstein 3 051004	3/24/05	4/4/05	4/11/05	^{90}Sr	1.10 ± 0.37	0.68	**S(+,-)**
Guernsey 6 051005	3/24/05	4/4/05	4/11/05	^{90}Sr	-0.55 ± 0.93	0.50	**S(+,-), U, Q**
Jersey 8 051006	3/25/05	4/4/05	4/11/05	^{90}Sr	1.55 ± 0.37	0.61	**S(+,-)**
							QC Test Qualifiers[1]
Guernsey 1 DU 051008	4/4/05	4/4/05	4/11/05	^{90}Sr	1.95 ± 0.38	0.85	
Batch Blank 051009	4/4/05	4/4/05	4/11/05	^{90}Sr	-0.43 ± 0.66	1.3	E, Q*
LCS 051007	4/4/05	4/4/05	4/11/05	^{90}Sr	12.81 ± 0.49	1.5	**S(+)**
Jersey 8 MS 051010	4/4/05	4/4/05	4/11/05	^{90}Sr	15.50 ± 0.51	1.6	**S(-)**

Matrix Spike: 20.0 pCi/L added.
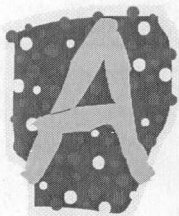LCS Target: 10.0 pCi/L
Analysis by Liquid Scintillation Counting
Critical Level ~ 0.6 pCi/L

Approved by: I. M. Wright, QA Officer

*The grayed-out qualifiers in the final column (E, Q) are present only as part of this exercise. These qualifiers generally would NOT be applied to the QC samples. This is particularly true for the matrix spike and the LCS where the MDC is relatively unimportant when the measured concentraiton is obviously real. The E that was added in the sample section indicates that the MDC required in the APS of 1.0 pCi/L was not met. In this case, the E may or may not be retained by the data validator.

TABLE 4.2 — Crosswalk between project plan document elements and directed planning process

ID	Project Plan Document Elements (QAPP—EPA, 2001)*	Content	Directed Planning Process Input
A – PROJECT MANAGEMENT			
A1	Title and Approval Sheet	Title and approval sheet.	
A2	Table of Contents	Document control format.	
A3	Distribution List	Distribution list for the plan document revisions and final guidance.	Include the members of the project planning team and stakeholders.
A4	Project/Task Organization	1) Identify individuals or organizations participating in the project and discuss their roles and responsibilities. 2) Provide an organizational chart showing relationships and communication lines.	The directed planning process: • Identifies the stakeholders, data users, decisionmakers. • Identifies the core planning team and the technical planning team members responsible for technical oversight. • Identifies the specific people/organizations responsible for project implementation (sampling and analysis).
A5	Problem Definition/ Background	1) State the specific problem to be solved and decision to be made. 2) Include enough background to provide a historical perspective.	Project planning team: • Documents the problem, site history, existing data, regulatory concerns, background levels and thresholds. • Develops a decision statement.
A6	Project/Task Description	Identify measurements, special requirements, sampling and analytical methods, action levels, regulatory standards, required data and reports, quality assessment techniques, and schedules.	Project planning team identifies: • Deadlines and other constraints that can impact scheduling. • Existing and needed data inputs. Project planning team establishes: • Action levels and tolerable decision error rates that will be the basis for the decision rule. • The optimized sampling and analytical design as well as quality criteria.
A7	Quality Objectives and Criteria for Measurement Data	1) Identify DQOs, data use, type of data needed, domain, matrices, constraints, action levels, statistical parameters, and acceptable decision errors. 2) Establish MQOs that link analysis to the user's quality objectives. 3) APSs. 4) Method validation requirements.	Project planning team: • Identifies the regulatory standards and the action level(s). • Establishes the decision rule. • Describes the existing and needed data inputs. • Describes practical constraints and the domain. • Establishes the statistical parameter that is compared to the action level. • Establishes tolerable decision error rates used to choose quality criteria. • Establishes quality criteria linked to the optimized design. • Establishes data verification, validation and assessment criteria and procedures. • Establishes APSs and MQOs.

1

TABLE 4.2 (Continued) — Crosswalk between project plan document elements and directed planning process

ID	Project Plan Document Elements (QAPP—EPA, 2001)*	Content	Directed Planning Process Input
A8	Special Training Requirements/ Certification	Identify and discuss special training/certificates required to perform work.	Project planning team: • Identifies training, certification, accreditation requirements for field and laboratory. • Identifies federal and state requirements for certification for laboratories. • Identifies federal and state requirements for activities, such as disposal of field-generated residuals.
A9	Documentation and Record	Itemize the information and records, which must be included in a data report package including report format and requirements for storage etc.	Project planning team: • Indicates whether documents will be controlled and the distribution list incomplete. • Identifies documents that must be archived. • Specifies period of time that documents must be archived. • Specifies procedures for error corrections (for hard copy and electronic files).
B – MEASUREMENT/DATA ACQUISITION			
B1	Sampling Process Designs (Experimental Designs)	(1) Outline the experimental design, including sampling design and rationale, sampling frequencies, matrices, and measurement parameter of interest. (2) Identify non-standard methods and validation process.	Project planning team establishes the rationale for and details of the sampling design.
B2	Sampling Methods Requirements	Describe sampling procedures, needed materials and facilities, decontamination procedures, waste handling and disposal procedures, and include a tabular description of sample containers, sample volumes, preservation and holding time requirements.	Project planning team specifies the preliminary details of the optimized sampling method.
B3	Sample Handling and Custody Requirements	Describe the provisions for sample labeling, shipment, sample tracking forms, procedures for transferring and maintaining custody of samples.	Project planning team describes the regulatory situation and site history, which can be used to identify the appropriate sample tracking level.
B4	Analytical Methods Requirements	Identify analytical methods and procedures including needed materials, waste disposal and corrective action procedures.	Project planning team: • Identifies inputs to the decision (nuclide of interest, matrix, etc.). • Establishes the allowable measurement uncertainty that will drive choice of the analytical protocols. • Specifies the optimized sampling and analytical design.

2

ID	Project Plan Document Elements (QAPP—EPA, 2001)*	Content	Directed Planning Process Input
B5	Quality Control Requirements	(1) Describe QC procedures and associated acceptance criteria and corrective actions for each sampling and analytical technique. (2) Define the types and frequency of QC samples should be defined along with the equations for calculating QC statistics.	Project planning team: • Establishes the allowable measurement uncertainty, which will drive QC acceptance criteria. • Establishes the optimized analytical protocols and desired MQOs.
B6	Instrument/Equipment Testing Inspection and Maintenance Requirements	1) Discuss determination of acceptable instrumentation performance. 2) Discuss the procedures for periodic, preventive and corrective maintenance.	
B7	Instrument Calibration and Frequency	(1) Identify tools, gauges and instruments, and other sampling or measurement devices that need calibration. (2) Describe how the calibration should be done.	Project planning team establishes the desired MQOs, which drive acceptance criteria for instrumentation performance.
B8	Inspection/Acceptance Requirements for Supplies and Consumables	Define how and by whom the sampling supplies and other consumables will be accepted for use in the project.	
B9	Data Acquisition Requirements (Non-direct Measurements)	Define criteria for the use of non-direct measurement data such as data that come from databases or literature.	Project planning team: • Identifies the types of existing data that are needed or would be useful. • Establishes the desired MQOs that would also be applicable to archived data.
B10	Data Management	(1) Outline of data management scheme including path of data, use of storage and& record keeping system.(2) Identify all data handling equipment and procedures that will be used to process, compile, analyze the data, and correct errors.	
C – ASSESSMENT/OVERSIGHT			
C1	Assessments and Response Actions	(1) Describe the number, frequency and type of assessments needed for the project. (2) For each assessment: list participants and their authority, the schedule, expected information, criteria for success and unsatisfactory conditions and those who will receive reports and procedures for corrective actions.	Project planning team establishes the MQOs and develops statements of the APSs, which are used in the selection of the analytical protocols and in the ongoing evaluation of the protocols.
C2	Reports to Management	Identify the frequency, content and distribution of reports issued to keep management informed.	

3

ID	Project Plan Document Elements (QAPP—EPA, 2001)*	Content	Directed Planning Process Input
D – DATA VALIDATION AND USABILITY			
D1	Data Review, Verification and Validation Requirements	State the criteria including specific statistics and equations, which will be used to accept or reject data based on quality.	Project planning team: • Establishes the MQOs for the sample analysis, and may also discuss completeness and representativeness requirements that will be the basis of validation. • Establishes the action level(s) relevant to the project DQOs. • Establishes the data validation criteria.
D2	Verification and Validation Methods	Describe the process to be used for validating and verifying data, including COC for data throughout the lifetime of the project.	Project planning team: • Determines appropriate level of custody. • May develop a validation plan.
D3	Reconciliation With Data Quality Objectives	Describe how results will be evaluated to determine if DQOs are satisfied.	Project planning team: • Defines the necessary data input needs. • Defines the constraints and boundaries with which the project has to comply. • Defines the decision rule. • Identifies the hypothesis and tolerable decision error rates. • Defines MQOs for achieving the project DQOs.

[Adapted from: EPA, 2002]

* EPA QAPP elements are discussed in MARLAP Appendix D, *Content of Project Plan Documents*

U. S. Environmental Protection Agency (EPA). 2002. *Guidance on Developing Quality Assurance Project Plans* (EPA QA/G-5). EPA/240/R-02/009. Office of Environmental Information, Washington, DC. Available at www.epa.gov/quality/qa_docs.html.

MARLAP TABLE E.6 — Example of a proposal evaluation plan

Proposal Evaluation

Objective: To ensure impartial, equitable, and comprehensive evaluation of proposals from contractors desiring to accomplish the work as outlined in the Request for Proposals and to assure selection of the contractor whose proposal, as submitted, offers optimum satisfaction of the government's objective with the best composite blend of performance, schedules, and cost.

Basic Philosophy: To obtain the best possible technical effort which satisfies all the requirements of the procurement at the lowest overall cost to the government.

Evaluation Procedures

1. Distribute proposals and evaluation instructions to Evaluation Committee.

2. Evaluation of proposals individually by each TEC member. Numerical values are recorded with a concise narrative justification for each rating.

3. The entire committee by group discussion prepares a consensus score for each proposal. Unanimity is attempted, but if not achieved, the Chairperson shall decide the score to be given.

4. A Contract Evaluation Sheet listing the individual score of each TEC member for each proposal and the consensus score for the proposal is prepared by the Chairperson. The proposals are then ranked in descending order.

5. The Chairperson next prepares an Evaluation Report which includes a Contract Evaluation Sheet, the rating sheets of each evaluator, a narrative discussion of the strong and weak points of each proposal, and a list of questions which must be clarified at negotiation. This summary shall be forwarded to the Contracting Officer.

6. If required, technical clarification sessions are held with acceptable proposers.

7. Analysis and evaluation of the cost proposal will be made by the Contracting Officer for all proposals deemed technically acceptable. The Chairperson of the TEC will perform a quantitative and qualitative analysis on the cost proposals or those firms with whom cost negotiations will be conducted.

Evaluation Criteria

The criteria to be used in the evaluation of this proposal are selected before the RFP is issued. In accordance with the established agency policy, TEC members prepare an average or consensus score for each proposal on the basis of these criteria and only on these criteria.

A guideline for your numerical rating and rating sheets with assigned weights for each criteria are outlined next under Technical Evaluation Guidelines for Numerical Rating.

MARLAP TABLE E.6 (Continued) — Example of a proposal evaluation plan

Technical Evaluation Guidelines for Numerical Rating

1. Each item of the evaluation criteria will be based on a rating of 0 to 10 points. Therefore, each evaluator will score each item using the following guidelines:

   a. *Above normal*: 9 to 10 points (a quote element which has a high probability of exceeding the expressed RFP requirements).

   b. *Normal*: 6 to 8 points (a quote element which, in all probability, will meet the minimum requirements established in the RFP and Scope of Work).

   c. *Below normal*: 3 to 5 points (a quote element which may fail to meet the stated minimum requirements, but which is of such a nature that it has correction potential).

   d. *Unacceptable*: 0 to 2 points (a quote element which cannot be expected to met the stated minimum requirements and is of such a nature that drastic revision is necessary for correction).

2. Points will be awarded to each element based on the evaluation of the quote in terms of the questions asked.

3. The evaluator shall make no determination on his or her own as to the relative importance of various items of the criteria. The evaluator must apply a 0 to 10 point concept to each item without regard to his or her own opinion concerning one item being of greater significance than another. Each item is given a predetermined weight factor in the Evaluation Plan when the RFP is issued and these weight factors must be used in the evaluation.

Consolidated Recommendations from MARLAP, Part I

2.8 Project Planning Process

1. MARLAP recommends the use of a directed project planning process.

2. MARLAP recommends that the radioanalytical specialists be a part of the integrated effort of the project planning team.

3. MARLAP recommends that the planning process rationale be documented and the documentation integrated with the project plan documents.

4. MARLAP recommends using a graded approach in which the sophistication, level of QC and oversight, and resources applied are appropriate to the project.

3.8 Key Analytical Planning Issues and Developing Analytical Protocol Specifications

5. 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.

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

7. 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.

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

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

10. 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.

11. 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.

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

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

4.7 Project Plan Documents

14. MARLAP recommends using a graded approach to project plan writing because of the diversity of environmental data collection activities.

15. MARLAP recommends developing a primary integrating project plan that includes other documents by citation or as appendices.

16. MARLAP recommends developing project plan documents that integrate all technical and quality aspects for the life-cycle of the project, including planning, implementation, and assessment.

17. MARLAP recommends including, by citation or as an appendix, the report on the directed planning process in the project plan documents.

18. If the planning process was not documented in a report, MARLAP recommends that a summary of the planning process addressing assumptions and decisions, established action levels, the DQO statement, and APSs (which include the established MQOs and any specific analytical process requirements) be included in the project plan documents.

19. MARLAP recommends using a formal process to control and document changes if updates of the original project plan document are needed.

5.6 Obtaining Laboratory Services

20. MARLAP recommends that technical specifications be prepared in writing in a single document, designated a SOW, for all radioanalytical laboratory services, regardless of whether the services are to be contracted out or performed by an Agency's laboratory.

21. MARLAP recommends that the MQOs and analytical process requirements contained in the SOW be provided to the laboratory.

22. MARLAP recommends that the SOW include the specifications for the action level and the required method uncertainty for the analyte concentration at the action level for each analyte/matrix.

23. MARLAP recommends that the laboratory submit the proposed methods and required method validation documentation with the formal response.

24. MARLAP recommends that the RFP state that subcontracting will be permitted only with the contracting organization's approval.

25. MARLAP recommends that all members of the TEC have a technical understanding of the subject matter related to the proposed work.

6.11 Selection and Application of an Analytical Method

26. MARLAP recommends the performance-based approach for method selection.

27. MARLAP recommends that only methods validated for a project's application be used.

28. MARLAP recommends that a SOW containing the MQOs and analytical process requirements be provided to the laboratory.

29. MARLAP recommends that the SOW include the specifications for the action level and the required method uncertainty for the analyte concentration at the action level for each combination of analyte and matrix.

30. MARLAP recommends that a method undergo some basic general validation prior to project method validation.

31. MARLAP recommends that when a method is applied to a specific project, the method should then undergo validation for that specific application.

32. MARLAP recommends that as each new project is implemented, the methods used in the analysis of the associated samples undergo some level of validation. However, it is the project manager's responsibility to assess the level of method validation necessary.

33. MARLAP recommends a tiered approach for project method validation.

7.5 Evaluating Methods and Laboratories

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

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

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

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

38. MARLAP recommends that a MQO for method uncertainty be established for each

3

analyte/matrix combination.

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

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

8.7 Radiochemical Data Verification and Validation

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

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

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

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

9.8 Data Quality Assessment

45. MARLAP recommends that the assessment phase of a project (verification, validation, and DQA processes) be designed during the directed planning process and documented in the respective plans as part of the project plan documents.

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

47. MARLAP recommends the involvement of the data assessment specialist(s) on the project planning team during the directed planning process.

48. MARLAP recommends that the DQA process should be designed during the directed planning process and documented in a DQA plan.

49. MARLAP recommends that all sampling design and statistical assumptions be clearly identified in project plan documents along with the rationale for their use.

Plutonium Fabricators, Ltd.
Site Description

Plutonium Fabricators was a company whose principal product was making ^{241}Pu from ^{238}U. Their research group had discovered that bombardment of depleted uranium (DU) oxide with a select alpha energy range could produce ^{241}Pu via (α, n) reaction.

The DU targets were dissolved in acid and the ^{241}Pu was extracted, transformed to the oxide and sold as a source. The remainder of the target was reconstituted for further production of the plutonium. The reconstitution process involved solvent extraction (using xylene and tri-n-octyl phosphine oxide), uranium oxide precipitation, and high-temperature firing of the precipitate.

Two processing storage facilities (Buildings "U" and "P"; see Figure 1) were built below grade (at different depths) to perform the reprocessing and contain the waste solutions from the extraction processes. The company used tanks and barrels for storage of solutions within the "U" and "P" buildings. After 15 years of operation, the tanks in the lowest level of the "P" building were found to be leaking. It was also noted at that time that the building foundation was cracked. Company engineering personnel were unable to determine the age of the cracks or for how long the tanks had been leaking.

The reprocessed uranium material was fired in the "U" building. It was also discovered that an oven exhaust duct had developed a significant leak. This caused some particulate uranium oxide to be distributed throughout the building. Ground water leaking into the "U" building compounded the problem of concrete contamination. The ground water spread out the contamination and allowed seepage into the concrete.

The company temporarily ceased production of ^{241}Pu focusing their efforts on minimizing the spread of contamination. During this cleanup phase the company went bankrupt. The major source term materials have been removed from the site (i.e., the leaking tanks and barrels).

> **You have been assigned as the project manager for the assessment of the ground-water contamination. Your task is to write an analytical protocol specification (APS) for each of the radionuclides potentially present in the ground water.**

The site has had 10 sampling wells placed, which are equidistant from the midpoint of the two buildings (Figure 1). These wells are sampled (4 liters each) monthly. The flow of ground water radiates from directly below the building equally in all directions. All stakeholders have agreed that the average of the 10 monthly samples around the site will be used to assess the ^{241}Am concentration with respect to the action level.

These wells have already been sampled and shown to contain ^{241}Pu, the parent of ^{241}Am, as well as naturally occurring uranium and thorium (plus decay products) in concentrations less than 5 pCi/L. There will be continued monitoring for the plutonium. The current goal is to determine if the concentration of ^{241}Am in the ground water (on average) is greater than 15 pCi/L. Since the closure of the plant four years ago, ground water measurements of all wells gave ^{241}Pu values ranging from 10 to 100 pCi/L. If a monthly average concentration exceeds the action level, stakeholders have agreed that the sampling frequency will be increased to weekly.

1

The ground-water chemistry is identified in the table below:

pH	Specific Conductivity	Na (ppm)	Ca (ppm)	Fe (ppm)	Dissolved Oxygen (ppm)	Turbidity (NTU)
8.5	520	120	35	3.4	0.1	50

Well location →

750 feet diameter

"U" Bldg   "P" Bldg

Admin Bldg

120 feet
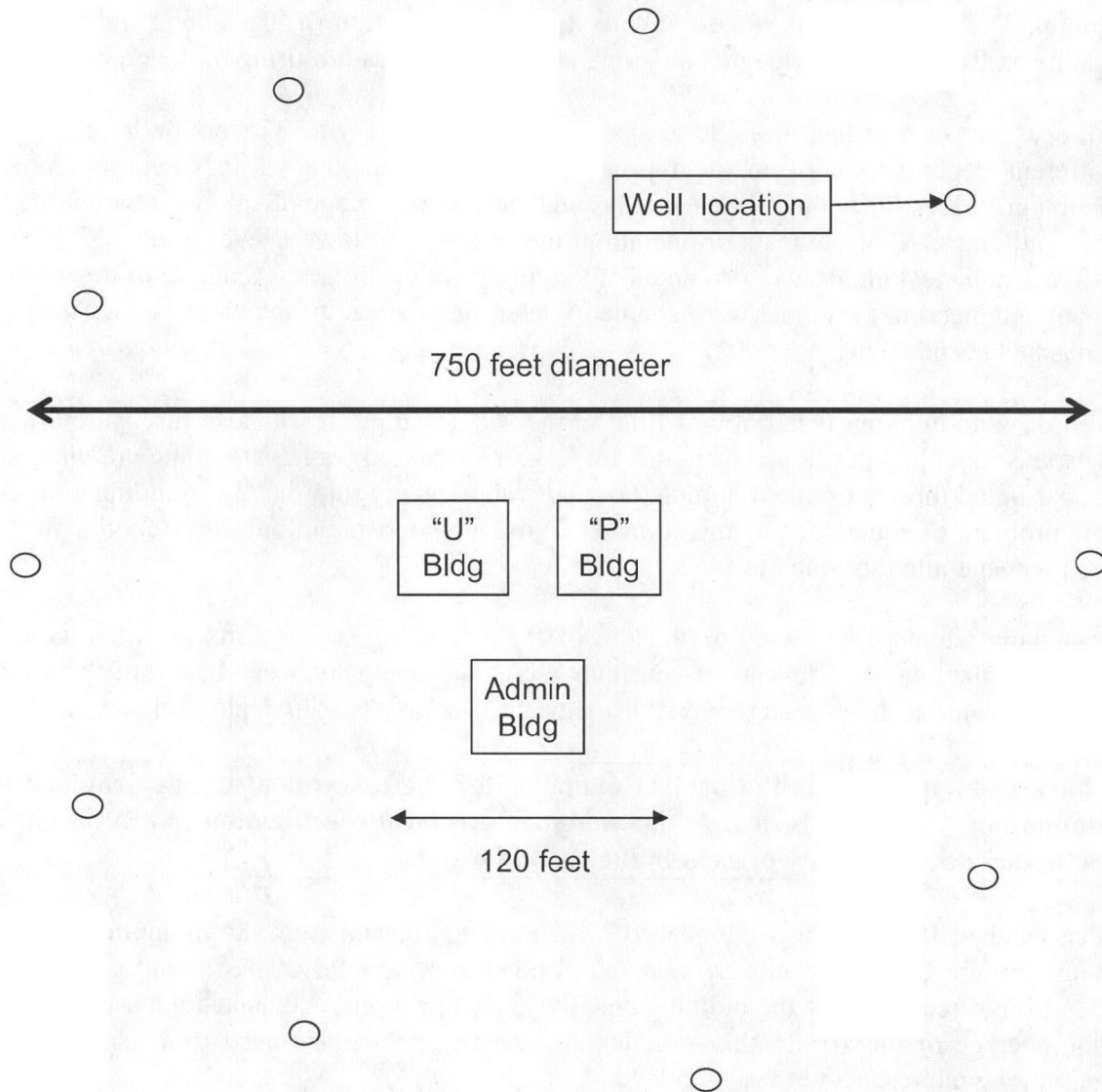
Figure 1. Schematic of Plutonium Fabrication Facility

2

Delineating the Gray Region and Determining the Required Method Uncertainty

1) What is the population parameter to be estimated from the data to be obtained?

   $\bar{x}$ ^{241}Am in Gw sample from 10 wells

2) What is the population from which the samples will be taken? _IU amthly sample further-to-mo_

   All poss 4-L samples from 10 wells

Use this information to fill in the x-axis title and show the following on the graph:

3) What is the action level? 15 pci/l **MDL**

4) What is the discrimination level (i.e. the lower bound on the gray region)?

   [5] [MDL]

5) What are the alternative decisions?

   $\uparrow \leftarrow$ $^{241}Am > 15$ (show N)

   $^{241}Am \leq 15$

6) Decision Rule:

   If $^{241}Am > 15 \rightarrow$ fw monit

Delineating the Gray Region

7) Null Hypothesis: $\bar{x} \leq AL$

8) Alternative Hypothesis: $\bar{x} > AL$

9) What is the desired limit on the probability of making a decision error if the true concentration is at the DL? 0.05   Type —

10) What is the desired limit on the probability making a decision error if the true concentration is at the AL? 0.05   type —

11) Using this imformation, what is the required method uncertainty for your project to meet these goals?

$$\frac{AL - DL}{10}$$

3

Analytical Protocol Specifications
(Template from MARLAP Chapter 3, Figure 3.2)

Analyte List: ^{241}Am by α-spec

Analysis Limitations:

Matrix: H2O w/ TSS

Possible Interferences: ^{237}NP, ^{237}U

Concentration Range: 0 – 100 (arb)

Action Level: 15 pci/ℓ

Method Validation Requirements: Level B or D that cover two applications: method for same matrix and newly developed or adapted method.

MQOs:

MUx = 1.5 pci/ℓ at 15 pci/ℓ

QC Samples

Type	Frequency	Evaluation Criteria
method Blank	1/20	(To be completed later)
Matrix Spike	1/20	(To be completed later)
dupe (replicate)	1/20	(To be completed later)
		(To be completed later)

Analytical Process Requirements*

Activity	Special Requirements
Field Sample Preparation and Preservation	(To be completed later)
Sample Receipt and Inspection	(To be completed later)
Laboratory Sample Preparation	(To be completed later)
Sample Dissolution	(To be completed later)
Chemical Separations	(To be completed later)
Preparing Sources for Counting	(To be completed later)
Nuclear Counting	(To be completed later)
Data Reduction and Reporting	(To be completed later)
Sample Tracking Requirements	(To be completed later)
Other	(To be completed later)

*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.

Remediation of Plutonium Fabricators Ltd.

- Analytes of Interest: ^{241}Pu, ^{235}U, ^{234}U, ^{238}U, Total U, ^{241}Am
  For this exercise: ^{241}Am
- Other possible radionuclide interferences:
  ambient levels of ^{226}Ra (2 pCi/L) and ^{228}Ra (3 pCi/L) plus decay products including ^{210}Pb
  ^{238}U, ^{235}U, and ^{234}U plus short-lived decay products
  ^{241}Pu with some ^{237}Np and ^{237}U
- Matrix: ground water with some solids (50 NTU) from monitoring wells located around the site and background locations
- Action level: 15 pCi/L – EPA Regulations – use for evaluating the mean of the sample population
- Required detection level: 1.5 pCi/L from EPA regulations; use for detectability for individual samples
- Estimated sample load: 20 samples per week
- Sample size: ~ 4 liters
- Required turnaround time: 30 days
- Contract specification: 10% pricing penalty for late results
- ^{241}Am Characteristics
  $t_{1/2}$ = 432.2 years
  Radiation emission: α ; 5.443 and 5.485 MeV
  Decay product: ^{237}Np - α, $t_{1/2}$ = 2.1×10^6 years
  Oxidation state: +3 (Am^{+3})
  Other elemental considerations: most probable oxidation states:
  Ra and Pb as +2, Pu as +3, and possibly VI and U as VI
- ^{241}Pu Characteristics
  $t_{1/2}$ = 14.29 years
  Radiation emission: beta max. energy of 20.81 keV (99+%), alpha with energy of 4.89 MeV (2.4×10^{-3} %)
  Decay products: ^{241}Am by α, $t_{1/2}$ = 432.2 years, ^{237}U by β, $t_{1/2}$ = 6.8 days
  Anticipated oxidation state(s): +4 (Pu^{+4}), +3(Pu^{+3}) and possibly VI (PuO$_2$$^{+2}$) from nitric acid used for dissolving U targets and then heated
  Other elemental considerations: most probable oxidation states:
  Ra, Ca, and Pb as +2, Am as +3, U as VI

Important Considerations for the Project Manager:
- Has this radionuclide been analyzed by this laboratory?
- Has it been analyzed at the detection levels needed for the project?
- Has the laboratory ever encountered this specific matrix and do they have a specific procedure for treating this matrix?
- Has the laboratory performed this radionuclide analysis with the type of interferents (stable or radioactive) known to exist in your sample?
- Does the laboratory procedure specifically identify the interferents?
- Has the laboratory analyzed this radionuclide in this matrix?
- Does the laboratory participate in a PE program for this radionuclide in this matrix?
- Does laboratory performance meet the project expectations?

Measurement Uncertainty
EXERCISE

Introduction: Your lab analyzes water samples for ^{241}Am by alpha-particle spectrometry, using chromatography to separate and purify the americium, and using microprecipitation to prepare a filter source on a planchet for counting. Americium-243 is used as a tracer.

The full mathematical model for this measurement might be given by

$$c_a = \frac{N_{as}/t_s - N_{ab}/t_b}{N_{ts}/t_s - N_{tb}/t_b} \times \frac{c_t \times V_t \times D_t \times P_t}{V \times D_a \times P_a} \qquad (1a)$$

where

$c_a =$ activity concentration of ^{241}Am in the sample (the measurand)
$N_{as} =$ sample count in the ^{241}Am region of interest (ROI)
$N_{ab} =$ blank count in the ^{241}Am ROI
$N_{ts} =$ sample count in the ^{243}Am ROI
$N_{tb} =$ blank count in the ^{243}Am ROI
$t_s =$ sample count time
$t_b =$ blank count time
$c_t =$ ^{243}Am activity concentration of the tracer solution
$V_t =$ volume of tracer solution added to the sample aliquant
$D_t =$ correction factor for decay of ^{243}Am from the tracer reference date through counting
$P_t =$ alpha emission probability for the ^{243}Am ROI
$V =$ volume of the sample aliquant analyzed
$D_a =$ correction factor for decay of ^{241}Am from sample collection through counting
$P_a =$ alpha emission probability for the ^{241}Am ROI

For simplicity in this example, since the decay factors tend to be very close to 1, we will omit them. We will also assume that the alpha emission probabilities are exactly 1 (with no spillover outside each ROI). So we'll use Equation 1b as our model.

$$c_a = \frac{N_{as}/t_s - N_{ab}/t_b}{N_{ts}/t_s - N_{tb}/t_b} \times \frac{c_t \times V_t}{V} \qquad (1b)$$

We will assume the count times t_s and t_b have negligible uncertainty. We'll consider only the uncertainty components due to N_{as}, N_{ab}, N_{ts}, N_{tb}, c_t, V_t, and V.

Problem: (1) Using the information presented below, calculate each of the seven aforementioned uncertainty components. (2) Use the results from step 1 to calculate the combined standard uncertainty of the output estimate, c_a. (3) Use the coverage factor $k = 2$ to calculate the expanded uncertainty, U. (4) Format the result and its expanded uncertainty as they might be presented to a client using one of the common shorthand notations discussed earlier.

Input	Value	Uncertainty information
N_{as}	21	Poisson (low level), $u(N_{as}) = \sqrt{N_{as} + 1}$
N_{ab}	1	Poisson (low level), $u(N_{ab}) = \sqrt{N_{ab} + 1}$
N_{ts}	892	Poisson (low level), $u(N_{ts}) = \sqrt{N_{ts} + 1}$
N_{tb}	2	Poisson (low level), $u(N_{tb}) = \sqrt{N_{tb} + 1}$
t_s	36 000 s	Negligible uncertainty
t_b	60 000 s	Negligible uncertainty
c_t	3346 pCi/L	$U = 72$ pCi/L ($k = 2$) . $u = 36$
V_t	1 mL, or 0.001 L	$u(V_t) = 0.004$ mL, or 4×10^{-6} L
V	0.15000 L	$u(V) = 0.00075$ L

Assumptions:
- None of the input estimates are correlated with each other.
- Dead time is negligible.
- Peaks in the alpha spectrum are cleanly separated, and there is no spillover from either ROI.
- Subsampling uncertainty is negligible for this water sample.
- Historical QC data indicate no significant amount of ^{241}Am contamination in method blank samples.
- We choose to ignore the decay-correction factors.

The output estimate (the activity concentration of ^{241}Am) is calculated below.

$$c_a = \frac{N_{as}/t_s - N_{ab}/t_b}{N_{ts}/t_s - N_{tb}/t_b} \times \frac{c_t \times V_t}{V}$$

$$= \frac{21/(36000\ \text{s}) - 1/(60000\ \text{s})}{892/(36000\ \text{s}) - 2/(60000\ \text{s})} \times \frac{(3346\ \text{pCi/L}) \times (0.001\ \text{L})}{0.15000\ \text{L}}$$

$$= 0.510\ 839\ 695\ \text{pCi/L}$$

Notice that we haven't tried to round the result yet. That will happen later.

(1) The sensitivity coefficients have been calculated for you in the table below. Use the information on the previous page to fill in the standard uncertainty of each of the seven input estimates and calculate the associated component of the combined standard uncertainty, $u_i(y)$, in the fourth column of the table.

Input estimate x_i	Sensitivity coefficient $c_i = \partial f / \partial x_i$	Standard uncertainty $u(x_i)$	Component of $u_c(y)$ generated by $u(x_i)$ $u_i(y) = \|\partial f / \partial x_i\| \times u(x_i)$ pCi/L	Square of $u_i(y)$ $u_i^2(y)$ pCi^2/L^2
N_{as}	0.025041161503 pCi/L	$\sqrt{21+1} = \sqrt{22}$ $^{4.69}$	0.1174	0.01379
N_{ab}	−0.015024696902 pCi/L	$\sqrt{1+1} = \sqrt{2} = 1.41$	0.02115	4.47E-4
N_{ts}	−5.734617138 × 10^{-4} pCi/L	$\sqrt{893} = 29.9$	$171 \times 10^{-4} = 0.0171$	0.0002924
N_{tb}	3.440770283 × 10^{-4} pCi/L	$\sqrt{3} = 1.73$	$5.959 = 0.0005959$	3.55E-7
c_t	1.526717557 × 10^{-4}	$72/2 = 36$	$54.94 = 0.0005494$	3E-5
V_t	510.8396947 pCi/L^2	4E-6	0.204	0.0416
V	−3.405597964 pCi/L^2	7.5E-4	0.00255	6.5E-6
			Combined variance $u_c^2(c_a)$:	0.05622

0.01458 ⟵ Ractual

(2) Use the uncertainty propagation formula to calculate the combined variance of c_a. For this exercise, just square each of the seven uncertainty components calculated in the fourth column of the table above, write the results in the last column, add them up, and write the sum in the lower right corner. (This sum is the combined variance of c_a.) Then calculate the combined standard uncertainty by taking the square root of the combined variance.

$$u_c(c_a) = \sqrt{u_c^2(c_a)} = \underline{\quad 0.05622 \quad} \text{ pCi/L}$$

(3) Calculate U by multiplying $u_c(c_a)$ by the coverage factor ($k = 2$).

$$U = \left(k \times u_c(c_a)\right) = \underline{\quad 0.237 \quad} \text{ pCi/L}$$

(4) Finally, round the result (0.510 839 695 pCi/L) and its expanded uncertainty, and write them in the appropriate shorthand format.

$$\underline{\quad 0.51 \pm 0.24 \text{ pci/l} \quad}$$

Procedure XYZ 15-10: Analysis of Liquid Samples for ^{241}Am by Gamma Spectrometry

Introduction

Analysis for ^{241}Am in groundwater samples can be performed by utilizing its gamma ray emission line at 59 keV. Sample count time is 25,000 seconds for a 4-L Marinelli beaker, to achieve a minimum detectable concentration (MDC) of 1.5 pCi/L. Water samples shall have been preserved by adding sufficient concentrated nitric acid to a 4-L Marinelli beaker so that the pH of the sample is less than 2.0. Sample acidification is important so that americium does not precipitate out during the long count times required to achieve the required MDC.

References

1. Procedure XYZ 1-1 QA Program for Gamma Spectrometric Analysis.
2. USNRC Regulatory Guide 4.15.
3. MARLAP. 2004. Multi-Agency Radiological Laboratory Analytical Protocols Manual. Volumes 1–3. Washington, DC: EPA 402-B-04-001A-C, NUREG 1576, NTIS PB2004-105421.

Precautions

1. New Marinelli beakers shall be used for each new sample.
2. Only Detectors 1 and 2 can achieve the stated MDC for ^{241}Am in 25,000 seconds. Detectors 4, 5, and 6 require at least 35,000 seconds. All count times must be adjusted to accommodate these detectors.
3. A daily background shall be performed prior to the start of each batch of samples. Daily background counts are 15,000 seconds per detector.
4. Acidification of groundwater samples generally requires 15 mL of concentrated nitric acid. The solution pH must be verified to be < 2.0 before commencing the gamma spectrometric analysis.
5. A matrix spike sample shall be run with each batch. The spike added to the unknown shall be sufficient ot bring the final concentration of the solution to > 30 pCi/L.

Procedure

1. Transfer approximately 2 L of sample to the 4-L Marinelli beaker.
2. Add 15 mL of concentrated nitric acid.
3. Transfer enough sample to bring the Marinelli beaker to the mark designated "4 L."
4. Using a stirring rod and pH paper, verify that the pH of the solution is less than 2.0. If pH is $\geq$ 2.0 add an additional 10 mL of concentrated nitric acid and repeat the pH measurement.
5. Place the lid snugly on the Marinelli beaker, "burp" the container, and seal the lid interface with electrical tape.
6. Wipe the outside of the Marinelli beaker with a dry cloth.
7. Place the Marinelli beaker on the detector can, close the cave, and put up the "in use" flag.
8. Enter the preset count time according to the detector selected (see Precautions).
9. When the count is finished verify the following parameters on the gamma ray printout sheets:
    a. Detector
    b. Count time for the detector used to achieve an MDC of 1.5 pCi/L
    c. Sample size
    d. The Sample date
    e. The count date
    f. MDC for ^{241}Am is $\leq$ 1.5 pCi/L if no gamma ray peak is identified.
10. Log the values for each sample in the client folder on the LABDATA system. Values that are below the MDC should be logged as "zero."

1

Final Conditions
1. All samples shall be disposed of in the containers marked "Acid Waste."
2. Each detector shall be inspected for cleanliness following each sample counting period.

Laboratory XYZ Method W04
Radiochemical Analysis of ^{241}Am in Water by Alpha Spectrometry
Abbreviated Method with Major Detail

1.	Scope
1.1	This procedure describes a method for separation and quantification of americium in water.

2.	Summary of Method
2.1	A calcium phosphate precipitation technique is used to concentrate and remove actinides from water samples. Americium is separated by extraction chromatography from other actinides prior to measurement by alpha spectrometry. Sequential extraction chromatography uses a CMPO-TBP resin column to remove actinides (Ac, Th, Pa, U, Np, Pu) and lanthanides (La, Ce, etc.) from the sample. Americium and the lanthanides are eluted from the column. If excessive lanthanides are in the sample, an Aliphatic Quaternary Amine resin column is used to separate americium from the lanthanides. A ^{243}Am radiotracer is used to monitor chemical yield and correct results to improve accuracy.

3.	Interferences
3.1	Actinides with unresolvable alpha energies such as ^{241}Am and ^{238}Pu must be chemically separated to enable ^{241}Am quantification. This method separates these radionuclides effectively.
3.2	Very high levels of phosphate in the sample may cause a chemical interference. Adjusting the amount of phosphate added to coprecipitate the actinides may be necessary in these cases.

4.	Apparatus - see detailed procedure W04

5.	Reagents - see detailed procedure W04

6.	Procedure
6.1.	*Water Sample Preparation:*
6.1.1.	If required, filter a 1L sample through a 0.45 micron filter.
6.1.2.	Add 5 mL of concentrated HCl (sp gr 1.19) per L of sample (0.5 mL per 100 mL) to acidify each sample.
6.1.3.	Add appropriate tracers and/or analyze standards per lab protocol.
6.1.4.	*Calcium phosphate precipitation option:*
6.1.4.1	Add 0.5 mL of 1.25M Ca(NO$_3$)$_2$ to each beaker.
6.1.4.2	Allow the samples to heat until boiling.
6.1.4.3	Once the samples boil, add 2-3 drops of phenolphthalein indicator and 200 µL of 3.2M (NH$_4$)$_2$HPO$_4$ solution.
6.1.4.4	Add enough concentrated NH$_4$OH with a squeeze bottle to reach the phenolphthalein end point and form Ca$_3$(PO$_4$)$_2$ precipitate.
6.1.4.5	Separate the precipitate from solution by decanting the supernatant
6.1.4.6	Transfer the precipitate to a centrifuge tube and centrifuge the precipitate for approximately 10 minutes at 2000 rpm.
6.1.4.7	Decant supernatant and discard to waste.
6.1.4.8	Wash the precipitate with an amount of water approximately twice the volume of the precipitate. Mix well on a vortex mixer. Centrifuge for 5-10 minutes. Discard the supernatant.

6.1.4.9   Dissolve precipitate in approximately 5 mL concentrated nitric acid. Transfer solution to a 100 mL beaker. Rinse centrifuge tube with 2-3 mL of concentrated nitric acid and transfer to beaker. Evaporate solution to dryness.

6.2.   *Am/La Separations using extraction chromatographic resins:*

6.2.1   *Redissolve calcium phosphate precipitate:*

6.2.1.1   Dissolve each precipitate with 10 mL of 3M HNO_3-1M $Al(NO_3)_3$.

6.2.1.2   Add approximately 200 mg of ascorbic acid to each solution, swirling to mix.

6.2.2   *Am Separation Using a CMPO-TBP Extraction Resin:*

6.2.2.1   For each sample dissolved, place a CMPO-TBP Resin column in the column rack.

6.2.2.2   Pipet 5 mL of 2M HNO_3 into each column to condition resin and allow to drain.

6.2.2.3   Transfer each solution from step 6.2.1.2 into the appropriate CMPO-TBP Resin column by pouring and/or using a plastic transfer pipet.

6.2.2.4   Allow the load solution to drain through column.

6.2.2.5   Pipet 5 mL of 2M HNO_3 into the sample beaker and transfer this rinse to the appropriate column using the same plastic transfer pipet. Allow to drain.

6.2.2.6   Pipet 5 mL of 2 M HNO_3- 0.1 M $NaNO_2$ directly into each column, rinsing each column reservoir while adding the 2 M HNO_3- 0.1 M $NaNO_2$.
Note: Sodium nitrite is used to oxidize Pu+3 to Pu+4 and enable the Pu/Am separation

6.2.2.7   Add 5 mL of 0.5M HNO_3 to each column and allow to drain.
Note: 0.5M HNO_3 is used to lower the nitrate concentration prior to conversion to the chloride system.

6.2.2.8   Discard the load and rinse solutions to waste.

6.2.2.9   Ensure that clean, labeled beakers or vials are below each column.

6.2.2.10   Add 3 mL of 9M HCl to each column to convert to chloride system. Collect eluate.

6.2.2.11.   Add 20 mL of 4M HCl to elute americium. Collect eluate in same beaker. Set beakers aside for Am/La separation option 6.2.3

6.2.3   *Option: Separation of americium from lanthanides using Aliphatic Quaternary Amine Resin as required by significant lanthanides causing americium alpha spectral degradation:*

6.2.3.1   For each sample dissolved, place a Aliphatic Quaternary Amine column in the column rack.

6.2.3.2 - 6.2.3.14 steps - see detailed procedure.

6.2.3.15   Dissolve sample in 10 mL of 4M HCl

6.3   *Sample preparation for counting;*

6.3.1   Add 0.2 mL of cerium carrier to each beaker from step 6.2.3.15.

6.3.2   Add 1.0 mL of concentrated HF to each beaker. Swirl to mix. Let the solutions sit for at least 30 minutes before filtering.

6.3.3   Set up a 0.1 micron 25 mm filter, glassy side down on a Gelman filter apparatus, 50 mL polysulfide funnel and 100 mL polypropylene Erlenmeyer flask.

6.3.4   Add 3-5 mL of 80% ethanol to each filter, applying vacuum and ensuring there are no leaks along the sides. Add 2-3 mL of water to each filter.

6.3.5   Filter the sample and rinse 50 mL centrifuge tube with 5 mL water, transferring this rinse to the filter apparatus.

6.3.6   Wash each filter with 3-5 mL of ethanol.

6.3.7   Remove filters, place in plastic Petri dishes, and dry under (UV) lamps for a few minutes.

6.3.8   Mount filters on stainless planchets, using double-sided tape or glue stick and count by alpha spectrometry.

7.   Alpha Spectrometry Counting

7.1   Setup and perform an energy and efficiency calibration of the alpha spectrometry system according to the detailed Procedure W04.

7.2   Place the mounted sample on the appropriate calibrated shelf of the alpha spectrometer vacuum chamber.

7.3   Close the vacuum chamber door and initiate vacuum pump to slowly evacuate the chamber according to the detailed procedure W04.

7.4   Apply bias between the sample planchet and detector.

7.5   Apply detector bias and begin counting for a time period to meet MQO requirements.

8.   Calculations

8.1   Calculate ^{241}Am sample concentration and associated uncertainty, critical level and MDC according to the equations in the detailed procedure W04.

9.   Notes

9.1   *Bias* - A mean chemical yield of 95% has been reported for americium. Since results are corrected based on spike recovery, no significant bias should exist for the method.

References - See detailed procedure.

Laboratory XYZ Method Validation Data for Radiochemistry
Gamma Spectrometric Analysis of ^{241}Am in Ground Water

Introduction

Laboratory XYZ has performed gamma spectrometric analysis of groundwater samples previously, but has not had their gamma detector calibrated to 59 keV where the ^{241}Am gamma is located. Detector calibration was completed using a ^{241}Am source (NIST traceable), and a count time of 150 minutes for a 4 L sample.

The software method for gamma-ray analysis uses the region of interest (ROI) routine rather than a peak search algorithm. Each sample is counted for a period of 100 minutes, as are the blanks.

Aliquants from the NIST-traceable source were taken and appropriately diluted to 20, 10, and 5 pCi/L. Three of each of these solutions were made using laboratory demineralized water and nitric acid and placed in separate, new Marinelli beakers. These samples were analyzed according to Procedure XYZ 15-10 "Americium Analysis By Gamma Spectrometry" (this procedure and the detector calibration were newly created for this analysis).

Sample of ground water was spiked with the ^{241}Am standard and analyzed along with a set of blank samples. The blank samples were made from demineralized water and nitric acid to the same concentration of the samples and also placed in new Marinelli beakers.

Analysis results for the gamma spectrometric results of the samples' matrix spikes and blanks are shown below.

Data:

Method Validation Study

Nominal Concentrations	20 pCi/L		10 pCi/L		5 pCi/L	
Trial Number	pCi/L	$\pm 1\,\sigma$	pCi/L	$\pm 1\,\sigma$	pCi/L	$\pm 1\,\sigma$
1	23.4	1.1	14.8	1.6	9.5	1.6
2	22.5	1.5	13.9	1.3	8.6	1.8
3	21.8	1.3	14.3	1.4	9.3	1.6

Matrix Spike and Blanks

Sample	Blank 1	Blank 2	Blank 3	Spike Result	Spike added	Unspiked Value
pCi/L	0.55	0.83	0.77	45.7 ✗	40.0	-1.62
$\pm 1\sigma$	1.4✗	1.6✗	1.1✗	0.95	0.10	1.8✗

Rounded incorrectly

Method Validation Data Review Form

Nuclide: <u>Am-241</u>   Matrix: <u>Water</u>   Action Level _<u>15 pci/l</u>_

Laboratory Name: _____

Proposed Method: <u>XYZ 15-10 Americium Analysis by Gamma Spectrometry</u>

Required Method Validation Level: ___<u>B</u>___   Required Method Uncertainty: _<u>U$_{MR}$ 1.5 pci/l</u>_

Acceptance Criteria: Measured value within ±__2.8__× u$_{MR}$_ or ±_2.8_× φ$_{MR}$_10%_of known value (>1.5 pci)
                                                              ↳ 4.2   ↳

Data Evaluation:

Trial Number	Test Level 1 20 pCi/L (≤5.6)			Test Level 2 10 pCi/L ≤4.2			Test Level 3 5 pCi/L ≤4.2		
	Measured	|Δ|	Accepted Y/N	Measured	|Δ|	Accepted Y/N	Measured	|Δ|	Accepted Y/N
1	23.4	3.4	y	14.8	4.8	N	9.5	4.5	N
2	22.5	2.5	y	13.9	5.9	N	8.6	3.6	y
3	21.8	1.8	y	14.3	4.3	N	9.3	4.3	N
4									
5									
6									
7									

|Δ| = absolute value of difference between measured and known values

7

Laboratory XYZ Method Validation Data for Radiochemistry
Alpha Spectrometric Analysis of ^{241}Am in Ground Water

Introduction:

Laboratory XYZ had never analyzed ^{241}Am in water by radiochemistry on a routine basis. For this project, the laboratory downloaded, from a commercial web site, a widely used radiochemical method for ^{241}Am in water. The method was reviewed for project applicability and for laboratory instrumentation and equipment availability. The radiochemist at the laboratory decided to use the cerium fluoride microprecipitation rather than electrodeposition for the last purification step and final sample mounting for counting by the alpha spectrometer. Because this was a new method obtained from a nationally known method source, and had not previously been used by the laboratory, a method validation plan was established to test the method to meet Method Validation Level D.

Internal test samples were prepared by adding sufficient amounts of a NIST-traceable ^{241}Am aqueous solution to separate eight liter deionized water solutions (in high-density polyethylene containers) to obtain 20, 15, and 5 pCi/L concentrations. Prior to spiking, the solutions were made acidic by adding concentrated HCl (5 mL/L of sample). Seven 1 L samples were taken from each container and analyzed according to Procedure W04 (attached). A ^{243}Am radiotracer was used with each sample to determine the ^{241}Am chemical yield for the sample processed. Seven 1 L analytical blanks were prepared from acidified demineralized water (HCl) and were included as a fourth concentration level.

Analytical results for the alpha spectrometric measurements of the test samples and blanks are shown below.

Data:
Method Validation Study

Test Concentrations	20 pCi/L	15 pCi/L Action Level	5 pCi/L	0 pCi/L Blank
Trial Number	Measured pCi/L ± 1s			
1	20.6 ± 1.2	15.83 ± 0.97	5.22 ± 0.44	0.021 ± 0.013
2	19.1 ± 1.1	15.77 ± 0.97	4.57 ± 0.38	-0.015 ± 0.015
3	20.4 ± 1.2	14.25 ± 0.87	5.82 ± 0.49	0.031 ± 0.022
4	20.9 ± 1.2	13.73 ± 0.84	4.46 ± 0.38	0.010 ± 0.013
5	19.8 ± 1.1	14.78 ± 0.90	4.77 ± 0.40	0.013 ± 0.013
6	19.5 ± 1.1	15.31 ± 0.94	5.38 ± 0.45	-0.024 ± 0.013
7	20.6 ± 1.2	16.4 ± 1.0	6.32 ± 0.53	0.006 ± 0.013

eyeball → no bias

Method Validation Data Review Form

Nuclide: <u>Am-241</u>

Matrix: <u>Water</u>
Action Level <u>15 pci/l</u>

Laboratory Name: _____

Proposed Method: <u>W04 Radiochemistry with Alpha Spectrometry</u>

Required Method Validation Level: ____D____   Required Method Uncertainty: ____1.5 pci/l____

Acceptance Criteria: Measured value within ±__3__ × u_{MR} or ±__3__ × φ_{MR} _(10%)_ of known value

↳ 4.5

Data Evaluation:

Trial Number	Test Level 1 20 pCi/L ↳6			Test Level 2 15 pCi/L ≤4.5			Test Level 3 5 pCi/L ≤4.5		
	Measured	|Δ|	Accepted Y/N	Measured	|Δ|	Accepted Y/N	Measured	|Δ|	Accepted Y/N
1	20.6	0.6	Y	15.83	0.83	Y	5.22	0.22	Y
2	19.1	0.9		15.77	0.77		4.57	0.43	
3	20.4	0.4		14.25	0.75		5.82	0.82	
4	20.9	0.9		13.73	1.27		4.46	0.54	
5	19.8	0.2		14.78	0.22		4.77	0.23	
6	19.5	0.5		15.31	0.31		5.38	0.38	
7	20.6	0.6		16.4	1.4		6.32	1.32	

\|Δ\| = absolute value of difference between measured and known values

Laboratory XYZ

"We are the Wizards"

Project Name: Plutonium Fabricators, Ltd
Sample Date: September 1, 2005
Analysis Date: November 1, 2005
Analysis Method: Alpha Spectrometry, Method W04

Client ID	Laboratory ID	Sample Result (pCi/L)	1σ Uncertainty (pCi/L)	Qualifier
090105W1	1885P001	-0.002	0.067	U S+
090105W2	1885P002	4.97	0.33	S+
090105W3	1885P003	1.18	0.17	S+
090105W4	1885P004	12.61	0.52	S+
090105W5	1885P005	-0.011	0.065	U S+
090105W6	1885P006	22.7	2.6	Q S+ E
090105W7	1885P007	-0.007	0.066	U S+
090105W8	1885P008	6.66	0.38	S+
090105W9	1885P009	1.58	0.19	S+
090105W10	1885P010	0.90	0.15	S+
Matrix spike	1885PMS1-P002[1]	36.1	2.0	S+
LCS	1885PQC1[2]	26.1	1.7	S+ E
Blank	1885PB1	4.01	0.29	S+
Duplicate	1885PDP1-P008	11.66	0.50	S+

(handwritten annotation next to 090105W6 row: "valid because still > crit level")

1. Spike added to sample 1885P002 = 24.0 pCi/L
2. QC nominal value = 20.0 pCi/L

Calculate the critical value (L$_c$) for the samples in this data set according to the Project Plan Document as follows:

$$\text{Critical Value} = 1.645 \times 1\sigma$$

Where 1σ is the laboratory-reported uncertainty and the L$_c$ is based on the average value for the historical blanks.

I. For the Matrix Spike Result.

Calculate the "Z statistic" using the following equation:

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

SSR: Spiked sample result = ___36.1___
SR: Unspiked sample result = ___4.97___
SA: Spike concentration added = ___24___
φ_{MR}: Required *relative* method uncertainty above the action level (AL) expressed as a fraction: $\varphi_{MR} = [u_{MR} / AL] = $ ___10%___ ,

(1) SSR:__36.1__ - SR:__4.97__ - SA:__24__   =   __7.13__

(2) SSR^2:__1296__ + max(SR, AL):(__7.2__)^2 =   __1347__

(3) [from 2]^{½} = __36.7__ × φ_{MR}:__0.3__   =   __11__

(4) [from 1]: __7.13__ / [from 3]: __11__   =   Z:__0.66__   [<3]

II. Calculate the %D for the Laboratory Control Sample Using the Following Equation:

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

(1) SA: Spike concentration added as LCS   = __20__
(2) SSR: Measured Concentration of the LCS   = __26.1__
(3) SSR: __26.1__ - SA: __20__   = __6.1__
(4) %D = 100[from 3]/[from 1]   = __30.5__

Calculate the Control Limit % from:
      CL = 3 × φ_{MR} × 100 = 3 × __6.1__ × 100   = __30__ ,

2

III. For the Duplicate Result

Calculate the agreement based on the absolute value of the average of the two results as compared with the AL:

X_1: _6.66_

X_2: _11.66_

AL: _15_

φ_{MR}: _0.1_

$$X_{avg} = |X_1 + X_2|/2 = |\underline{6.66} + \underline{11.66}|/2 = |\underline{9.16}|$$

If $X_{avg} > $ AL then use

   Control Limit $= 4.24 \times \varphi_{MR} \times 100 = 4.24 \times$ _____ $\times 100 =$ _____

and compare the relative percent difference to the CL:

$$RPD = 100 \times \frac{|x_1 - x_2|}{\overline{X}}$$

If $\overline{X} < $ AL then use

   Control Limit $= 4.24 \times u_{MR} = 4.24 \times \underline{15} = \boxed{6.36}$

and compare the absolute difference to the CL:

   Absolute difference $= |X_1 - X_2|$ $\bigcirc 5$ $\rightarrow$ in control

IV. For the Laboratory Blank Sample:

The control limit for the balnk distribution is given by:

   Control Limit $= 3 \times u_{MR} = 3 \times (\underline{1.5}) = \underline{4.5}$

The value for the blank is compared to this limit. $Blk = 4.01 \rightarrow$ in control

Data Qualifiers
(MARLAP Chapter 8, Section 8.3.3)

Qualifiers Applied During Verification

E   Indicates that an exception or noncompliance has occurred. (This qualifier may be removed during the validation if evidence shows that this exception does not affect the sample results.)

Qualifiers Applied to Samples During Validation Based on Sample Results

U   Analytical result is less than the critical value; a nondetect.

Q   A reported measurement uncertainty that exceeds the required method uncertainty or relative method uncertainty (φ_{MR} or u_{MR}).

J   A result that is unusually uncertain or estimated.

R   A result that is rejected due to severe data problems.

Qualifiers Applied to Samples During Validation Based on QC Sample Results

S(+/-)   A LCS, MS, or MSD that is above (+) or below (-) the upper or lower control limit.

P   A sample result with its duplicate (replicate) that exceeds a control limit.

B(+/-)   A blank result that is outside the upper (+) or lower (-) control limit.