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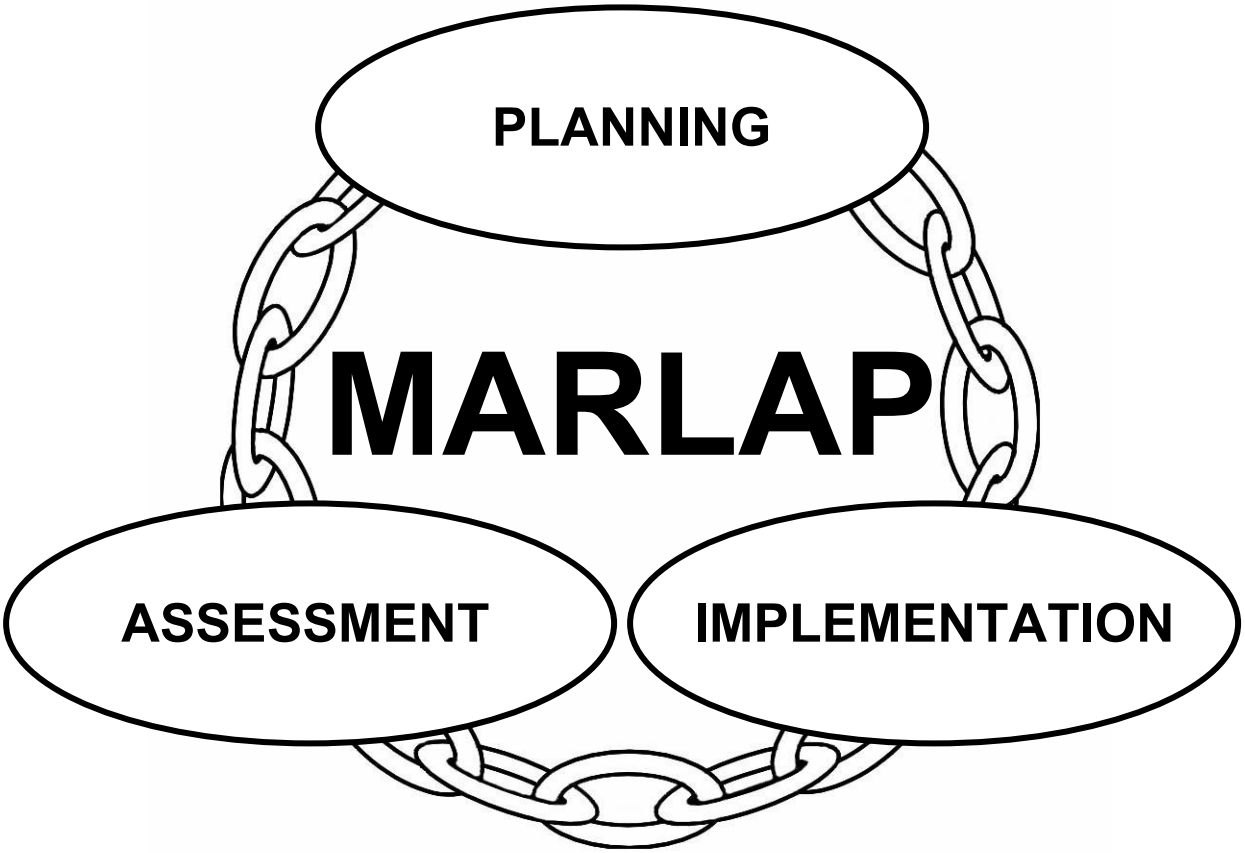
Multi-Agency Radiological Laboratory Analytical Protocols Manual

Volume III: Chapters 18 – 20 and Appendix G



July 2004

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Multi-Agency Radiological Laboratory Analytical Protocols Manual (MARLAP)

Part II: Chapters 18 – 20
Appendix G
(Volume III)

United States Environmental Protection Agency
United States Department of Defense
United States Department of Energy
United States Department of Homeland Security
United States Nuclear Regulatory Commission
United States Food and Drug Administration
United States Geological Survey
National Institute of Standards and Technology

July 2004

FOREWORD

MARLAP is organized into two parts. Part I, consisting of Chapters 1 through 9, is intended primarily for project planners and managers. Part I introduces the directed planning process central to MARLAP and provides guidance on project planning with emphasis on radioanalytical planning issues and radioanalytical data requirements. Part II, consisting of Chapters 10 through 20, is intended primarily for laboratory personnel and provides guidance in the relevant areas of radioanalytical laboratory work. In addition, MARLAP contains seven appendices—labeled A through G—that provide complementary information, detail background information, or concepts pertinent to more than one chapter. Six chapters and one appendix are immediately followed by one or more attachments that the authors believe will provide additional or more detailed explanations of concepts discussed within the chapter. Attachments to chapters have letter designators (e.g, Attachment "6A" or "3B"), while attachments to appendices are numbered (e.g., "B1"). Thus, "Section B.1.1" refers to section 1.1 of appendix B, while "Section B1.1" refers to section 1 of attachment 1 to appendix B. Cross-references within the text are explicit in order to avoid confusion.

Because of its length, the printed version of MARLAP is bound in three volumes. Volume I (Chapters 1 through 9 and Appendices A through E) contains Part I. Because of its length, Part II is split between Volumes II and III. Volume II (Chapters 10 through 17 and Appendix F) covers most of the activities performed at radioanalytical laboratories, from field and sampling issues that affect laboratory measurements through waste management. Volume III (Chapters 18 through 20 and Appendix G) covers laboratory quality control, measurement uncertainty and detection and quantification capability. Each volume includes a table of contents, list of acronyms and abbreviations, and a complete glossary of terms.

MARLAP and its periodic revisions are available online at www.epa.gov/radiation/marlap and www.nrc.gov/reading-rm/doc-collections/nuregs/staff/sr1576/. The online version is updated periodically and may differ from the last printed version. Although references to material found on a web site bear the date the material was accessed, the material available on the date cited may subsequently be removed from the site. Printed and CD-ROM versions of MARLAP are available through the National Technical Information Service (NTIS). NTIS may be accessed online at www.ntis.gov. The NTIS Sales Desk can be reached between 8:30 a.m. and 6:00 p.m. Eastern Time, Monday through Friday at 1-800-553-6847; TDD (hearing impaired only) at 703-487-4639 between 8:30 a.m. and 5:00 p.m Eastern Time, Monday through Friday; or fax at 703-605-6900.

MARLAP is a living document, and future editions are already under consideration. Users are urged to provide feedback on how MARLAP can be improved. While suggestions may not always be acknowledged or adopted, commentors may be assured that they will be considered carefully. Comments may be submitted electronically through a link on EPA's MARLAP web site (www.epa.gov/radiation/marlap).

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ACRONYMS AND ABBREVIATIONS

AC . . . . . alternating current
ADC . . . . . analog to digital convertor
AEA . . . . . Atomic Energy Act
AL . . . . . action level
AMS . . . . . accelerator mass spectrometry
ANSI . . . . . American National Standards Institute
AOAC . . . . . Association of Official Analytical Chemists
APHA . . . . . American Public Health Association
APS . . . . . analytical protocol specification
ARAR . . . . . applicable or relevant and appropriate requirement (CERCLA/Superfund)
ASL . . . . . analytical support laboratory
ASQC . . . . . American Society for Quality Control
ASTM . . . . . American Society for Testing and Materials
ATD . . . . . alpha track detector

BGO . . . . . bismuth germanate [detector]
BNL . . . . . Brookhaven National Laboratory (DOE)
BOA . . . . . basic ordering agreement

CAA . . . . . Clean Air Act
CC . . . . . charcoal canisters
CEDE . . . . . committed effective dose equivalent
CERCLA . . . . Comprehensive Environmental Response, Compensation, and Liability Act of 1980 ("Superfund")
c.f. . . . . carrier free [tracer]
cfm . . . . . cubic feet per minute
CFR . . . . . *Code of Federal Regulations*
CL . . . . . central line (of a control chart)
CMPO . . . . . [octyl(phenyl)]-N,N-diisobutylcarbonylmethylphosphine oxide
CMST . . . . . Characterization, Monitoring, and Sensor Technology Program (DOE)
CO . . . . . contracting officer
COC . . . . . chain of custody
COR . . . . . contracting officer's representative
cpm . . . . . counts per minute
cps . . . . . counts per second
CRM . . . . . (1) continuous radon monitor; (2) certified reference material
CSU . . . . . combined standard uncertainty
CV . . . . . coefficient of variation
CWA . . . . . Clean Water Act
CWLM . . . . . continuous working level monitor

d . . . . . day[s]
D . . . . . homogeneous distribution coefficient
DAAP . . . . . diamylamylphosphonate
DC . . . . . direct current
DCGL . . . . . derived concentration guideline level
DHS . . . . . U.S. Department of Homeland Security
DIN . . . . . di-isopropylnaphthalene
DL . . . . . discrimination limit
DoD . . . . . U.S. Department of Defense
DOE . . . . . U.S. Department of Energy
DOELAP . . . . DOE Laboratory Accreditation Program
DOT . . . . . U.S. Department of Transportation
DOP . . . . . dispersed oil particulate
dpm . . . . . disintegrations per minute
DPPP . . . . . dipentylpentylphosphonate
DQA . . . . . data quality assessment
DQI . . . . . data quality indicator
DQO . . . . . data quality objective
DTPA . . . . . diethylene triamine pentaacetic acid
DVB . . . . . divinylbenzene

E_e . . . . . emission probability per decay event
$E_{\beta max}$ . . . . . maximum beta-particle energy
EDD . . . . . electronic data deliverable
EDTA . . . . . ethylene diamine tetraacetic acid
EGTA . . . . . ethyleneglycol bis(2-aminoethylether)-tetraacetate
EMEDD . . . . . environmental management electronic data deliverable (DOE)
EPA . . . . . U.S. Environmental Protection Agency
ERPRIMS . . . Environmental Resources Program Management System (U.S. Air Force)
ESC . . . . . expedited site characterization; expedited site conversion
eV . . . . . electron volts

FAR . . . . . *Federal Acquisition Regulations*, CFR Title 48
FBO . . . . . *Federal Business Opportunities* [formerly *Commerce Business Daily*]
FDA . . . . . U.S. Food and Drug Administration
FEP . . . . . full energy peak
fg . . . . . femtogram
FOM . . . . . figure of merit
FWHM . . . . . full width of a peak at half maximum
FWTM . . . . . full width of a peak at tenth maximum

GC . . . . . gas chromatography
GLPC . . . . . gas-liquid phase chromatography
GM . . . . . Geiger-Mueller [detector]
GP . . . . . gas proportional [counter]
GUM . . . . . *Guide to the Expression of Uncertainty in Measurement* (ISO)
Gy . . . . . gray[s]

h . . . . . hour[s]
H_0 . . . . . null hypothesis
H_A, H_1 . . . . . alternative hypothesis
HDBP . . . . . dibutylphosphoric acid
HDEHP . . . . . bis(2-ethylhexyl) phosphoric acid
HDPE . . . . . high-density polyethylene
HLW . . . . . high-level [radioactive] waste
HPGe . . . . . high-purity germanium
HPLC . . . . . high-pressure liquid chromatography; high-performance liquid chromatography
HTRW . . . . . hazardous, toxic, and radioactive waste

IAEA . . . . . International Atomic Energy Agency
ICRU . . . . . International Commission on Radiation Units and Measurements
ICP-MS . . . . . inductively coupled plasma-mass spectroscopy
IPPD . . . . . integrated product and process development
ISO . . . . . International Organization for Standardization
IUPAC . . . . . International Union of Pure and Applied Chemistry

k . . . . . coverage factor
keV . . . . . kilo electron volts
KPA . . . . . kinetic phosphorimeter analysis

LAN . . . . . local area network
LANL . . . . . Los Alamos National Laboratory (DOE)
LBGR . . . . . lower bound of the gray region
LCL . . . . . lower control limit
LCS . . . . . laboratory control samples
LDPE . . . . . low-density polyethylene
LEGe . . . . . low-energy germanium
LIMS . . . . . laboratory information management system
LLD . . . . . lower limit of detection
LLNL . . . . . Lawrence Livermore National Laboratory (DOE)
LLRW . . . . . low-level radioactive waste
LLRWPA . . . . Low Level Radioactive Waste Policy Act

LOMI . . . . . low oxidation-state transition-metal ion
LPC . . . . . liquid-partition chromatography; liquid-phase chromatography
LS . . . . . liquid scintillation
LSC . . . . . liquid scintillation counter
LWL . . . . . lower warning limit

MAPEP . . . . . Mixed Analyte Performance Evaluation Program (DOE)
MARSSIM . . . *Multi-Agency Radiation Survey and Site Investigation Manual*
MCA . . . . . multichannel analyzer
MCL . . . . . maximum contaminant limit
MDA . . . . . minimum detectable amount; minimum detectable activity
MDC . . . . . minimum detectable concentration
MDL . . . . . method detection limit
MeV . . . . . mega electron volts
MIBK . . . . . methyl isobutyl ketone
min . . . . . minute[s]
MPa . . . . . megapascals
MQC . . . . . minimum quantifiable concentration
MQO . . . . . measurement quality objective
MS . . . . . matrix spike; mass spectrometer
MSD . . . . . matrix spike duplicate
MVRM . . . . . method validation reference material

NAA . . . . . neutron activation analysis
NaI(Tl) . . . . . thallium-activated sodium iodide [detector]
NCP . . . . . National Oil and Hazardous Substances Pollution Contingency Plan
NCRP . . . . . National Council on Radiation Protection and Measurement
NELAC . . . . . National Environmental Laboratory Accreditation Conference
NESHAP . . . . National Emission Standards for Hazardous Air Pollutants (EPA)
NIM . . . . . nuclear instrumentation module
NIST . . . . . National Institute of Standards and Technology
NPL . . . . . National Physics Laboratory (United Kingdom); National Priorities List (United States)
NRC . . . . . U.S. Nuclear Regulatory Commission
NRIP . . . . . NIST Radiochemistry Intercomparison Program
NTA (NTTA) . nitrilotriacetate
NTU . . . . . nephelometric turbidity units
NVLAP . . . . . National Voluntary Laboratory Accreditation Program (NIST)

OA . . . . . observational approach
OFHC . . . . . oxygen-free high-conductivity

OFPP . . . . . Office of Federal Procurement Policy

φ_{MR} . . . . . required relative method uncertainty
Pa . . . . . pascals
PARCC . . . . . precision, accuracy, representativeness, completeness, and comparability
PBBO . . . . . 2-(4'-biphenylyl) 6-phenylbenzoxazole
PCB . . . . . polychlorinated biphenyl
pCi . . . . . picocurie
pdf . . . . . probability density function
PE . . . . . performance evaluation
PERALS . . . . . Photon Electron Rejecting Alpha Liquid Scintillation®
PFA . . . . . perfluoroalcoholoxil™
PIC . . . . . pressurized ionization chamber
PIPS . . . . . planar implanted passivated silicon [detector]
PM . . . . . project manager
PMT . . . . . photomultiplier tube
PT . . . . . performance testing
PTB . . . . . Physikalisch-Technische bundesanstalt (Germany)
PTFE . . . . . polytetrafluoroethylene
PUREX . . . . . plutonium uranium reduction extraction
PVC . . . . . polyvinyl chloride

QA . . . . . quality assurance
QAP . . . . . Quality Assessment Program (DOE)
QAPP . . . . . quality assurance project plan
QC . . . . . quality control

rad . . . . . radiation absorbed dose
RCRA . . . . . Resource Conservation and Recovery Act
REE . . . . . rare earth elements
REGe . . . . . reverse-electrode germanium
rem . . . . . roentgen equivalent: man
RFP . . . . . request for proposals
RFQ . . . . . request for quotations
RI/FS . . . . . remedial investigation/feasibility study
RMDC . . . . . required minimum detectable concentration
ROI . . . . . region of interest
RPD . . . . . relative percent difference
RPM . . . . . remedial project manager
RSD . . . . . relative standard deviation
RSO . . . . . radiation safety officer

s . . . . . second[s]
SA . . . . . spike activity
S_C . . . . . critical value
SAFER . . . . . Streamlined Approach for Environmental Restoration Program (DOE)
SAM . . . . . site assessment manager
SAP . . . . . sampling and analysis plan
SEDD . . . . . staged electronic data deliverable
SI . . . . . international system of units
SMO . . . . . sample management office[r]
SOP . . . . . standard operating procedure
SOW . . . . . statement of work
SQC . . . . . statistical quality control
SPE . . . . . solid-phase extraction
SR . . . . . unspiked sample result
SRM . . . . . standard reference material
SSB . . . . . silicon surface barrier [alpha detector]
SSR . . . . . spiked sample result
Sv . . . . . sievert[s]

$t_{½}$ . . . . . half-life
TAT . . . . . turnaround time
TBP . . . . . tributylphosphate
TC . . . . . to contain
TCLP . . . . . toxicity characteristic leaching procedure
TD . . . . . to deliver
TEC . . . . . technical evaluation committee
TEDE . . . . . total effective dose equivalent
TEC . . . . . technical evaluation committee (USGS)
TES . . . . . technical evaluation sheet (USGS)
TFM . . . . . tetrafluorometoxil™
TIMS . . . . . thermal ionization mass spectrometry
TIOA . . . . . triisooctylamine
TLD . . . . . thermoluminescent dosimeter
TnOA . . . . . tri-n-octylamine
TOPO . . . . . trioctylphosphinic oxide
TPO . . . . . technical project officer
TPP . . . . . technical project planning
TPU . . . . . total propagated uncertainty
TQM . . . . . Total Quality Management
TRUEX . . . . . trans-uranium extraction
TSCA . . . . . Toxic Substances Control Act

TSDF . . . . . treatment, storage, or disposal facility
tSIE . . . . . transfomed spectral index of the external standard
TTA . . . . . thenoyltrifluoroacetone

U . . . . . expanded uncertainty
u_{MR} . . . . . required absolute method uncertainty
$u_c(y)$ . . . . . combined standard uncertainty
UBGR . . . . . upper bound of the gray region
UCL . . . . . upper control limit
USACE . . . . . United States Army Corps of Engineers
USGS . . . . . United States Geological Survey
UV . . . . . ultraviolet
UWL . . . . . upper warning limit

V . . . . . volt[s]

WCP . . . . . waste certification plan

XML . . . . . extensible mark-up language
XtGe® . . . . . extended-range germanium

y . . . . . year[s]
Y . . . . . response variable

ZnS(Ag) . . . . . silver-activated zinc sulfide [detector]

UNIT CONVERSION FACTORS

To Convert	To	Multiply by	To Convert	To	Multiply by
Years (y)	Seconds (s) Minutes (min) Hours (h)	3.16×10^{7} 5.26×10^{5} 8.77×10^{3}	s min h	y	3.17×10^{-8} 1.90×10^{-6} 1.14×10^{-4}
Disintegrations per second (dps)	Becquerels (Bq)	1.0	Bq	dps	1.0
Bq Bq/kg Bq/m^3 Bq/m^3	Picocuries (pCi) pCi/g pCi/L Bq/L	27.03 2.7×10^{-2} 2.7×10^{-2} 10^{3}	pCi pCi/g pCi/L Bq/L	Bq Bq/kg Bq/m^3 Bq/m^3	3.7×10^{-2} 37 37 10^{-3}
Microcuries per milliliter (µCi/mL)	pCi/L	10^{9}	pCi/L	µCi/mL	10^{-9}
Disintegrations per minute (dpm)	µCi pCi	4.5×10^{-7} 4.5×10^{-1}	pCi	dpm	2.22
Gallons (gal)	Liters (L)	3.78	Liters	Gallons	0.265
Gray (Gy)	rad	100	rad	Gy	10^{-2}
Roentgen Equivalent Man (rem)	Sievert (Sv)	10^{-2}	Sv	rem	10^{2}

18 LABORATORY QUALITY CONTROL

18.1 Introduction

This chapter addresses internal laboratory quality control (QC), the purpose of which is to monitor performance, identify problems, and initiate corrective action. If project requirements are more stringent than typical laboratory QC criteria, the project manager and the laboratory should confer to see whether the laboratory can accommodate the project QC requirements. Project QC requirements are addressed in Part I of MARLAP.

Laboratory data should be produced under a quality system[1] that incorporates planning, implementing, and internal assessment of the work performed by the laboratory, including QC. MARLAP fully endorses the need for a laboratory quality system and a quality manual that delineates the quality assurance (QA) policies and QC practices of the laboratory. A laboratory's quality system should ensure that laboratory processes and measurements are "in statistical control," which means that the distribution of measured results is stable.

This chapter's purpose is to provide guidance to laboratory staff on those activities and professional practices a radioanalytical laboratory should undertake to produce data of known quality. This chapter also shows how to use statistical techniques to monitor specific measures of the analytical process to indicate the level of control of the analytical process within the laboratory. These measures are called "performance indicators," and the statistical techniques involve the use of control charts. Monitoring performance indicators through control charts enables the identification of trends. The laboratory can then address analytical problems and help improve the analytical process. Section 18.3.2 and Attachment 18A at the end of this chapter provide examples of several types of charts. The use of statistical techniques is the preferred method for implementing quality control in the laboratory (Attachment 18B). The chapter also identifies specific performance indicators, the principles that govern their use, indications and underlying causes of excursions, statistical means of evaluating performance indicators, and examples of root-cause evaluations.

Contents

[1]A quality system is a structured and documented management framework that describes the policies, objectives, principles, organizational authority, responsibilities, accountability, and implementation plan of an organization for ensuring quality in its work processes, products (items), and services. The quality system provides for planning, implementing, and assessing the work performed by the organization and for carrying out required quality assurance and quality control (ANSI/ASQC E4, 1994). General requirements for testing laboratories can be found in ISO/IEC 17025.

This chapter addresses the control of the analytical process in the laboratory, as distinct from meeting the typical analytical needs of a specific project. Quality control provides quantitative estimates of analysis and measurement controls that can be used to determine compliance with project objectives.

18.1.1 Organization of Chapter

Chapter 18 has five major sections in addition to this introduction. Section 18.2 provides a general overview of QC and its application in the laboratory setting. Section 18.3 discusses the importance of evaluating performance indicators and provides statistical means for their evaluation. Sections 18.4 and 18.5 identify primary radiochemistry and instrumentation performance indicators, respectively, and discuss each in detail. Section 18.6 discusses other aspects of the analytical process that require scrutiny but are not formally considered performance indicators.

18.1.2 Format

The chapter is presented in a different format than the preceding chapters in order to highlight the performance indicators and to give examples. For each performance indicator, general guidance is provided in the format shown below.

Issue: Defines and summarizes the performance indicator

Discussion: Identifies those matters important to the performance indicator, including:

- What is the performance indicator and how does it work?
- Why is the performance indicator important, and what is its impact on the quality of the measurement?
- What is the relationship of the performance indicator and the combined standard uncertainty derived for the analytical method?
- What are the acceptable limits of the performance indicator?
- What are the key assumptions underlying the performance indicator?
- What limits and cautions are associated with the assumptions made?
- How sensitive is the quality of the measurement to the assumptions made?
- What is the appropriate frequency for assessing this performance indicator?

Excursions: "Excursions" are departures from the expected condition. This section addresses the likely types of excursions encountered during laboratory analysis and explains what each may indicate. This section also discusses the potential reasons for these excursions and the implications for the analytical results.

Examples: Where appropriate, this section provides typical examples of excursions, potential reasons for excursions, and additional information.

18.2 Quality Control

Quality control includes all technical activities that measure the attributes and performance of a process, item, or service against defined standards to verify that they meet the stated requirements established by the customer. It also includes operational techniques and activities that are used to fulfill requirements for quality (ANSI/ASQC E4, 1994).

QC may not always detect blunders. Good laboratory practices, in addition to adherence to standard operating procedures (SOPs), are part of the overall QA/QC aspects needed to check the laboratory's performance. To monitor and control quality, laboratories use performance indicators, which are instrument- or protocol-related parameters that are routinely monitored to assess the laboratory's estimate of measurement uncertainty, precision, bias, etc. Initially, these parameters are used to maintain or demonstrate control over the analytical process. The performance indicators should be tracked by appropriate personnel. If the performance indicator control limits are exceeded, management should be informed and corrective action should be initiated.

Figure 18.1 lists some of the potential causes for radioanalytical control excursions. By no means is the list complete, and the reader should be aware of additional potential causes of excursions that are presented in the rest of this chapter and the other chapters. Many problems are complex and have multiple components that could complicate the search for causes of protocol or instrument related excursions. A metrologist or radiochemist should be consulted to identify and remedy any analytical problems.

18.3 Evaluation of Performance Indicators

18.3.1 Importance of Evaluating Performance Indicators

As stated previously, performance indicators are measures of the analytical process that the laboratory monitors as part of its routine QC program. Performance indicators demonstrate whether the analytical process is performing as planned, when it has exhibited a statistical anomaly that requires investigation, and when a system has failed. Accordingly, monitoring performance indicators using established statistical techniques provides the laboratory with an effective tool for self assessment that allows the identification of trends or conditions that, while still within the established bounds of acceptability, are drifting or trending out of control. These conditions can be addressed prospectively, allowing the laboratory to maintain analytical control.

Additionally, this process allows the development of a data base regarding a protocol's or system's behavior over time or under a specified set of conditions.

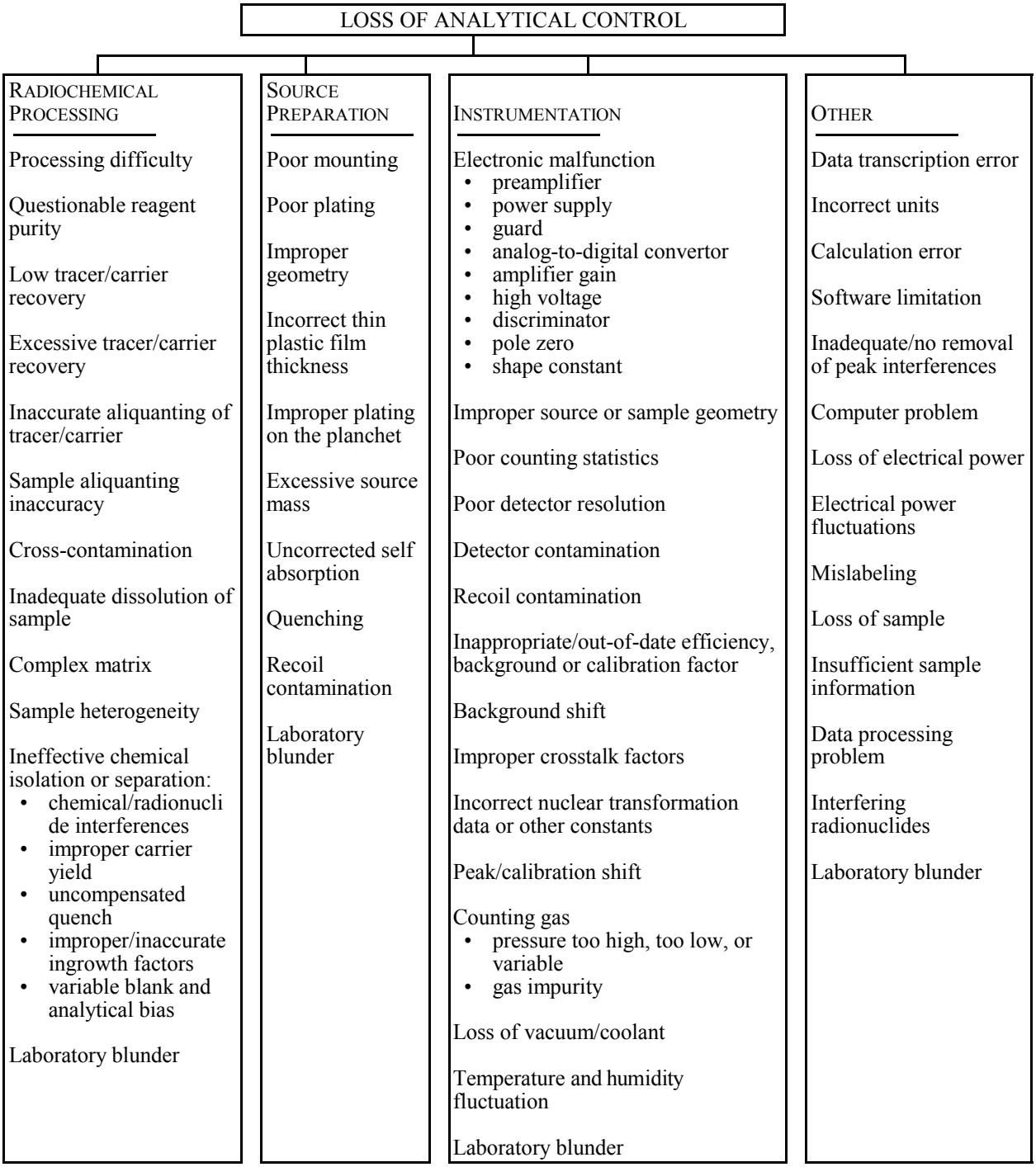

FIGURE 18.1 — Problems leading to loss of analytical control

18.3.2 Statistical Means of Evaluating Performance Indicators — Control Charts

The primary tool for statistical quality control is the control chart (see Attachment 18A). The theory that underlies a control chart is statistical hypothesis testing (see *NIST/SEMATECH e-Handbook of Statistical Methods*, http://www.itl.nist.gov/div898/handbook/, 2003). The implementation of a control chart makes the theory transparent to the average user and reduces the process of statistical inference to answering simple questions, such as, "Is the measured parameter greater than the upper control limit?" or "Is the measured parameter in the warning region?"

In theory, to test whether a parameter θ is above or below a certain value θ_0, a test statistic is defined and its distribution is determined under the assumption that $\theta = \theta_0$ (the null hypothesis). The value of the statistic is calculated and compared to critical values to test the assumption. In practice, a control chart is designed so that a non-statistician can perform these tests easily by comparing the measured value of the parameter to control limits and warning limits.

Most control charts do not implement hypothesis tests in a rigorous manner that allows decision error rates to be precisely determined. The charts are intended to be simple and practical tools for use even in situations where the assumptions needed for a rigorous test are not verifiable.

Every control chart has control limits, which define the acceptable range of the monitored variable. Many charts have both upper and lower limits. However, when changes in only one direction are of concern, only one limit is necessary. Most control charts have a central line, or reference line, which is an estimate of the expected value of the monitored variable. Many control charts also have warning limits, which lie between the central line and the control limits.

By definition, control limits are action limits. A single measured value that falls outside these limits normally requires that one stop the measurement process, investigate the problem, and if necessary take corrective action. The warning limits are optional but recommended, since they help one to identify and investigate possible problems before control limits are exceeded.

Types of Control Charts: Control charts based on grouped observations often are more powerful tools for detecting shifts of the monitored variable than charts based on individual observations. *Average charts*, or $\overline{X}$ *charts*, are used to monitor the arithmetic means of measured values obtained in "rational subgroups," which are subgroups of equal size chosen to ensure that the measurement variability within each subgroup is likely to represent only the inherent variability of the measurement process produced by non-assignable causes (see Attachment 18A). When an $\overline{X}$ chart is used, a *range chart*, or *R chart*, is generally used in tandem to monitor within-group variability. (The *range* of a set of values is the difference between the largest value and the smallest.)

A control chart for individual values (*X chart* or *I chart*) is used when it is impractical to obtain measured values in the groups needed for an $\overline{X}$ chart. In this case, a *moving range chart* (*MR chart*) is often used as well to monitor variability. The moving range chart is an R chart based on the absolute differences between consecutive measured values.

A control chart may or may not be based on a particular type of data distribution. Most control charts use limits derived from the normal distribution but are intended to be used for data with almost any distribution (ISO 8258). However, when data obtained from radiation counters are monitored, the Poisson distribution may often be assumed. The standard types of control charts for Poisson data in industrial applications are called "*c* charts" (for total counts) and "*u* charts" (for count rates). A third type of Poisson control chart, which is a variant of the *u* chart, is frequently used to monitor radiation counter efficiency. When the data distribution is Poisson, separate charts for monitoring the value of the parameter and its variability are generally unnecessary because the mean and variance of a Poisson distribution are numerically equal.

The following documents provide more guidance on the use of control charts:

- ASTM D6299. *Standard Practice for Applying Statistical Quality Assurance Techniques to Evaluate Analytical Measurement System Performance*.
- ASTM E882. *Standard Guide for Accountability and Quality Control in the Chemical Analysis Laboratory*.
- ANSI/ISO/ASQC A3534-2. *Statistics–Vocabulary and Symbols–Statistical Quality Control*.
- ISO 7870. *Control Charts – General Guide and Introduction*.
- ISO 7873. *Control Charts for Arithmetic Average with Warning Limits*.
- ISO 7966. *Acceptance Control Charts*.
- ISO 8258. *Shewhart Control Charts*.
- American Society for Testing and Materials (ASTM) MNL 7, *Manual on Presentation of Data and Control Chart Analysis* ASTM Manual Series, 7th Edition, 2002.

Figure 18.2 illustrates a typical control chart using counting data from analysis of a reference material (with limits corrected for decay) showing the statistical nature of the chart. The applicability of control chart techniques is based on the assumption that laboratory data approximate a normal distribution. The counting data plotted graphically represent the test results on the vertical axis and the scale order or time sequence in which the measurements were

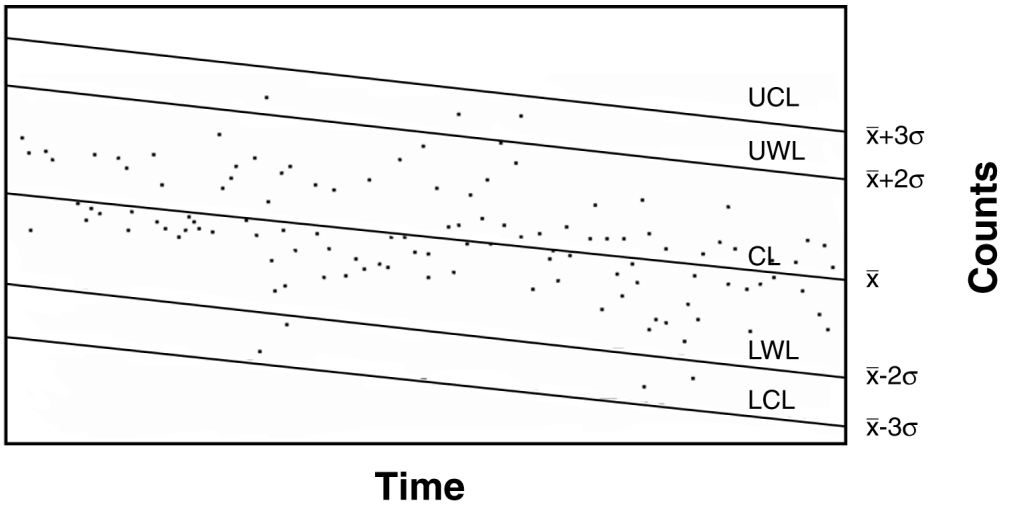

FIGURE 18.2 — Control chart for daily counting of a standard reference source, with limits corrected for decay

obtained on the horizontal axis. The mean of the measurements is represented by the central line (CL), and the limits of dispersion in terms of standard deviation are represented by the upper and lower warning and control limits (UWL, UCL, LWL, LCL). The warning limits are usually 2 standard deviations from the mean and the control limits are 3 standard deviations from the mean. See Attachment 18A for more discussion on establishing control charts.

18.3.3 Tolerance Limits

In some situations, the acceptance limits for a QC parameter may be based on professional judgment rather than statistics. MARLAP uses the term *tolerance limits* to refer to these judgment-based acceptance limits. (Note that this term has another meaning in statistics.) Tolerance limits are used much like the control limits on a control chart to determine whether investigation and corrective action are required. (They may also be called "go/no go limits.") Tolerance limits may be used when it is important to detect large changes in the variable. For example, tolerance limits could be used when variability within the limits has no significant impact on the measurement process.

An example of a variable that may sometimes appear to shift by small amounts is the resolution of a high-purity germanium detector. It also tends to be true that even statistically significant changes in the resolution are often so small that they have no practically significant effect on analytical results. So, it is reasonable to specify tolerance limits for the resolution (FWHM) rather than statistically based control limits.

Another example of a variable that is commonly monitored using tolerance limits is the chemical yield for an analytical process. Typically the yield is measured with relatively small uncertainty;

so, fluctuations of the yield over some range of values may have no substantial impact on the quality of the measurement. However, a yield that is significantly greater than 100 percent generally indicates a spurious error of some kind, and a yield that is very low may indicate a spurious error or other problem in the measurement process that deserves investigation (see Sections 18.6.4, "Interferences"; 18.6.5, "Negative Results"; and 18.6.7, "Calibration of Apparatus Used for Weight and Volume Measurements").

A graphical representation of the history of the monitored variable is useful even when control charts are not used. When the data are plotted on a graph with the tolerance limits drawn as lines (like the control limits on a control chart), the graph is sometimes called a *tolerance chart*.

18.3.4 Measurement Uncertainty

Issue: Every measured result is uncertain to some degree. If the measurement uncertainties are large relative to the tolerances needed for decision making, the data may not be useful for their intended purpose. A discussion of measurement uncertainty is contained in Chapter 19, and the terms used in this section are defined in that chapter and in the Glossary.

Discussion: In order to determine the significance of a sample result, all reported values should be accompanied by the laboratory's best estimate of the uncertainty associated with the result. The "combined standard uncertainty" (one-sigma uncertainty) is obtained by propagating the uncertainties of all the input quantities that contribute to the calculation of the derived value (Chapter 19).

The combined standard uncertainty is used to indicate the statistical confidence in interpreting the performance indicator's ability to assess analytical quality. The estimated statistical confidence level that is usually associated with 1 combined standard uncertainty is about 68 percent, the confidence level for 2 combined standard uncertainties is about 95 percent, and the confidence level for 3 combined standard uncertainties is about 99 percent. It is important that the combined standard uncertainty be a fair estimate because it will indicate when the analytical process could be approaching the limits of statistical control and corrective actions should be initiated. A performance indicator exceeding ±2 combined standard uncertainty limits from the indicator's historical mean value may indicate that corrective action should be considered, and a performance indicator exceeding ±3 combined standard uncertainty limits from the indicator's historical mean value may indicate that an investigation must be conducted and corrective action may be necessary. Because statistical confidence never reaches 100 percent, it probably would be prudent to confirm the measurement for the performance indicator when it exceeds ±2 combined standard uncertainty limits. If the performance indicator value for repeat measurements do not exceed ±2 combined standard uncertainty limits, one may conclude that the first measurement was a statistically allowable event. However, if the excursion is repeated, appropriate investigative actions should be considered.

Most of the significant sources of uncertainty in radiochemical data are known to a laboratory and can be estimated. These include uncertainties associated with sample and background counting, radiochemical yield determination, efficiency calibration, and blank assessment. Other less easily defined but significant sources of uncertainty include those associated with self-absorption and quench correction, sample density correction, sample geometry variation, gamma photopeak area determination, determination of sample volume or weight, and dead time correction.

The uncertainty of a measured value is controllable, within certain limits, by decreasing the uncertainty associated with some input parameters. For samples containing low levels of radioactivity, a large component of the combined standard uncertainty may be associated with the instrumental assessment (counting) of the sample aliquant, i.e., the standard uncertainty of the net count (gross sample count minus background count). Increasing the total net count accumulated, or decreasing the uncertainty of the instrument background, or both, will decrease the counting uncertainty. Changes that may be made to decrease the counting uncertainty include increasing the counting time for the sample or background, increasing the sample aliquant size (unless the sample geometry, quench, or self-absorption factors offset the gain in total radioactivity counted), using a more efficient geometry or detector, using an instrument with a lower background, and reanalyzing the sample to obtain a greater radiochemical yield. It also may be possible to concentrate the sample, which has the equivalent effect of increasing the sample aliquant size.

18.4 Radiochemistry Performance Indicators

Section 18.3 discussed how to evaluate radiochemistry performance indicators using statistically based control chart techniques. Any of the indicators below (blanks, replicates, laboratory control samples, matrix spikes, certified reference material, or tracer yield) can be evaluated using the control chart techniques. Analysts can use numerical performance indicators to identify loss of control. Control charts will assist laboratory personnel in identifying the quality trends and excursions of any performance indicator.

18.4.1 Method and Reagent Blank

Issue: A method blank is a sample of a matrix as similar as practical to the associated samples that is free from the analytes (radionuclides) of interest to the extent possible. The method blank is processed simultaneously with, and under the same conditions as, samples through all steps of the analytical procedures. A reagent blank consists of the analytical reagent(s) in the procedure without the target analyte or sample matrix, introduced into the analytical procedure at the appropriate point and carried through all subsequent steps to determine the contribution of the reagents and of the involved analytical steps.

Blank samples are used to determine whether any radionuclide contamination is introduced by the measurement process. They assist in the control of any contamination introduced by the

laboratory. Ideally, no target analytes should be present in the blank at detectable concentrations. If that is not possible (e.g., for naturally occurring radionuclides), those radionuclides should be extremely well-characterized and tracked. Control charts can be used to track these radionuclide levels in blanks. Using *X* charts, the laboratory can establish a program that evaluates the levels and trends of radionuclides in the different laboratory blanks. The techniques for establishing such a control chart program are described in Attachment 18A.

Discussion: The method blank is assumed to be representative of all samples in the batch with respect to the matrix and contamination assessment. When practical, it consists of the same or equivalent medium as the analytical samples, such as a deionized water blank for aqueous samples. Soil blanks are often prepared using "clean sand," commercially available fine-grained or beach sand whose inherent concentrations of target radionuclides are small and have been characterized sufficiently by the laboratory to allow its use as a blank. This approach may not be appropriate for very low-level analyses. Powdered, natural-matrix Standard Reference Materials (SRMs) are commercially available from the National Institute of Standards and Technology (NIST) and also may be suitable (Section 18.4.5). However, due to the natural variability of soils, each choice of method blank medium must be evaluated by the laboratory prior to use. The results of method blanks typically are not used to correct sample activities but only to monitor for contamination.

Reagent blanks are matrix-independent and assess any contamination only from the reagents and lab-ware. They may be used to correct sample activities for the contribution of naturally occurring radionuclides in the reagents, and used like method blanks, to check for unexpected contamination. The results of the reagent blank analyses should be reported separately by the analytical laboratory. How their values are used in determining the final sample results should be addressed during the final data assessment.

It is common practice for some laboratories to add the reagents into a volume of deionized water equal to the sample volume, while other laboratories simply add the required reagents to an empty container and process it as an analytical sample. In either case, it should be noted that the reagent blank is not monitoring the entire analytical process. The fundamental issue for each laboratory is to decide on the appropriate reagent blank necessary to obtain the needed information on the measurement system. Considerable variability exists among laboratories in the use and preparation of reagent blanks.

In general, the reagent blank's concentration of analyte is expected to be small compared to that of the sample. However, for some low-activity environmental samples this may not be the case, and the correction becomes increasingly important as the concentration of the analyte in the sample approaches background concentrations. In these cases, care should be taken to accurately quantify the levels of radionuclides in the reagent blanks.

It is important to minimize radionuclide concentrations in the blanks and bring these levels under control. This is usually achieved through careful selection of reagents, maintaining laboratory and counting areas free from contamination, and by segregating high and low activity samples. Thorough documentation of all blank values is essential to allow for the application of statistical tests to evaluate potentially anomalous values and delineate their extent.

Ideally, the analyte concentration in a method or reagent blank should be as close to zero as possible, and replicate measurement of the blanks should be consistent within counting statistics. Acceptance criteria for blank results should be established and applied to all data, and should include warning and control limits (Section 18.3.2, "Statistical Means of Evaluating Performance Indicators — Control Charts"). Blank values require scrutiny as part of the data evaluation and validation process for each analytical batch. Should restocking of reagents or other wholesale laboratory changes occur during a project, the method and reagent blanks prepared under the new conditions should be re-evaluated to ensure that they continue to be within established criteria.

An example of a numerical performance indicator for a method blank or a reagent blank used to monitor for unexpected contamination is

$$Z_{\text{Blank}} = \frac{x}{u_c(x)} \tag{18.1}$$

where x denotes the measured blank activity and $u_c(x)$ denotes its combined standard uncertainty. Warning limits for Z_{Blank} are ±2 and control limits are ±3. As mentioned earlier, if a reagent blank is used to blank-correct sample results, the blank results should be evaluated using control charts.

Typically, one method blank and/or reagent blank is analyzed with each batch or grouping of analytical samples regardless of batch size. Situations may occur where more frequent blanks are required to ensure that analytical conditions are stable, particularly when analyzing high and low concentration samples in the same analytical batch, or when instruments, reagents, or analytical method are suspect.

In general, corrective actions include procurement control of reagents, good laboratory cleaning practices, sample segregation according to anticipated concentrations, and instrument-related concerns, as discussed in this section. Good laboratory cleaning protocols should incorporate the evaluation of method and reagent blank performance to indicate if current practices are adequate. Instrument background data indicate a system's stability, and can be used to pinpoint the source of contamination, as can routine contamination (removable and fixed) surveys of laboratory and counting areas that are performed by the organization's health physics or radiation safety personnel.

Excursion: Blank changes can be grouped into three general categories: rapid changes, gradual increase or decrease, and highly variable changes. These are represented in Figure 18.3 and described below.

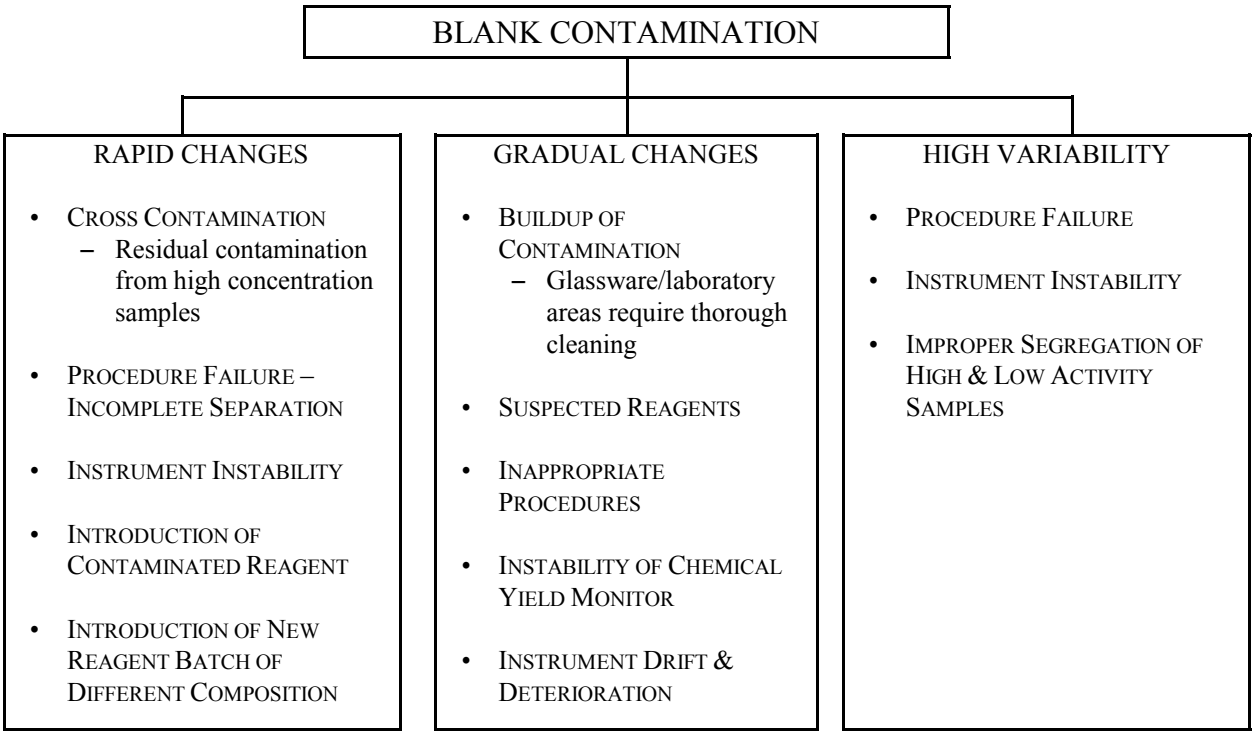

FIGURE 18.3 — Three general categories of blank changes

Rapid Changes: A sudden change in a blank value indicates the existence of a condition requiring immediate attention. Sudden changes often are caused by the introduction of a contaminant from high concentration samples, impure reagents, or contaminated sample preparation areas. Two potential sources of increased values in blanks are laboratory cleaning practices and contaminated reagents. A laboratory protocol should be established for cleaning and monitoring contamination from laboratory ware and equipment. Laboratory reagents, either as newly prepared solutions or from newly opened bottles, also can be a source of unexpected contamination. Significant increases in blank radioactivity should suggest these two as possible sources, and if confirmed, they should be corrected. Particular attention should be paid to the samples analyzed directly prior to the contaminated blank, since small amounts of residues from these samples can contaminate the instrument and have large effects on subsequent results when analyzing samples at or near environmental background. It may be necessary to take swipe or smear samples of questionable areas to identify the contaminant's source followed by a thorough cleaning or decontamination of all affected areas. Additionally, method or reagent blank values that are suddenly depressed should be investigated and may indicate other problems, including instrument malfunction like a loss of counting gas, incomplete chemical separation during the chemical preparation, or the failure to add necessary reagents. These other problems may be reflected in other areas, such as instrument performance checks or tracer yields.

Gradual Changes: Gradually increasing blank values indicate the need to inspect all sample preparation and counting areas for sources of residual contamination. Often housekeeping or routine contamination control details such as cleaning glassware or instrument counting chambers are sufficient to bring blank values under control. Alternatively, gradually decreasing blank values warrant scrutiny with respect to proper instrument settings and procedural related problems like a lack of tracer/sample exchange, failure of chemical separation reactions, or the addition of all necessary reagents. The importance of documenting method and reagent blank values in this regard cannot be overemphasized, since data evaluation and trending analyses are impossible without complete records.

High Variability: Because method blank values are expected to be near zero, the degree of variability they exhibit should reflect the statistical variation inherent in determinations near these levels. Large variations in blank values typically indicate problems related to instruments or the analytical process, as discussed in the two previous sections.

18.4.2 Laboratory Replicates

Issue: A laboratory replicate is two or more aliquants taken at the first subsampling event, normally after homogenization. In the event that there is no subsampling (when the method calls for using the entire sample) replicate analysis typically involves counting the prepared sample twice. The results of laboratory replicates are used to evaluate the method precision. Note that counting a sample twice only assesses the instrument portion of the measurement process.

Precision is a measure of agreement among replicate measurements of the same property under prescribed similar conditions. Precision is a fundamental aspect of the analytical process and should be evaluated routinely as part of the laboratory's quality system. Evaluation typically is performed using multiple analysis of the same sample (blanks, spikes, blinds, reference materials, performance evaluation samples, etc.), in whole or part, and evaluating the analyses relative to a statistically based criterion. The range of sample types requires that the sample matrix's effects on the precision be captured and evaluated by the laboratory's routine quality control practices. The reproducibility of analytical results should be evaluated by replicates to establish this uncertainty component.

Discussion: The purpose for measuring precision is to determine whether the laboratory can execute an analytical method consistently and thus obtain results of acceptable variability. Analytical samples cover a range of physical forms or matrices, from homogeneous samples like finished drinking water to complex soils or heterogeneous wastes, and each matrix has the potential to affect a protocol's precision.

In general, precision for aqueous samples tends to be less affected by sample heterogeneity than other media because if the sample's constituents are dissolved the sample is essentially homo-

geneous. This facilitates dividing the samples into equivalents fractions or aliquants. When appropriate, acidification of a sample to pH less than 2 should be done prior to dividing it for replicate analysis. Multi-phase and high-solid-content samples that are heterogeneous are more problematic.

The acceptance criterion for precision should be related to the combined standard uncertainties of the measured results. The uncertainty of a result may depend on many factors (e.g., dissolved solids in water or particle sizes of soil), but such factors should affect the acceptance criterion only through their effect on the standard uncertainty.

As an alternative to sample duplicates, a matrix spike duplicate is sometimes used as an indicator of the reproducibility of the analytical precision, as discussed in Section 18.4.3. A matrix spike duplicate is treated in the same manner as an unspiked replicate: both samples (original and duplicate) are processed identically to the other samples in the batch, and each aliquant is treated as an individual sample.

If the sample has multiple phases, the phases should be separated for individual analysis. For heterogenous materials, multiple analyses should be used, or the combined standard uncertainty of the results should be increased, to account for subsampling error (Appendix F). A typical frequency for replicate analyses is a minimum of one per analytical batch, regardless of batch size. "Batch" is defined as a given number of samples of similar matrix type with associated QC samples analyzed under the sample conditions at approximately the same time.

All analytical batches should be evaluated with respect to precision, whether by using replicates or matrix spike duplicates. This is done typically by the use of an acceptance criterion that derives a statistic that quantifies the difference between two values obtained by analyzing the same sample. Limits are then placed on the criterion, and data for any batch in excess of the criterion require investigation and corrective action as appropriate. An example of a numerical performance indicator for laboratory replicates is

$$Z_{\text{Rep}} = \frac{x_1 - x_2}{\sqrt{u_c^2(x_1) + u_c^2(x_2)}} \tag{18.2}$$

where x_1 and x_2 denote the two measured activity concentrations and $u_c(x_1)$ and $u_c(x_2)$ denote their respective combined standard uncertainties. Warning limits for Z_{Rep} are ±2 and control limits are ±3.

Excursions: A regularly scheduled evaluation of precision with respect to the acceptance criterion should be an integral part of the laboratory quality system. Careful attention should be paid to the nature and anticipated analyte concentrations of all samples processed by the laboratory. Prospective identification of samples where precision is expected to be problematic often

can address difficulties in this area. The choice of appropriate analytical method and analyst training are also important. An analyst needs to be familiar with specific steps in the procedure that provide an indication of incomplete processing.

Precision exhibits a range of values and depends in part on sample matrix and activity, assuming correct execution of the analytical method. Small changes, positive and negative, are expected and should be captured in the acceptance criterion's range. It is also sensitive to sample heterogeneity or errors in processing, such as incomplete chemical separation or sample dissolution, and lack of tracer or carrier equilibration. When performance indicators for precision are outside acceptance criteria, the laboratory should determine the reasons why and implement corrective actions.

Certain samples will exhibit higher variability because of their matrix, or the proximity of their analyte concentration to ambient background, as discussed previously. Consideration should be given to cases where a matrix requires the development and implementation of a specific acceptance criterion. The main causes for lack of precision (Figure 18.4) can be grouped as follows:

- Laboratory subsampling — subsampling techniques produced two dissimilar aliquants from one sample, and the original and duplicate are not the same. An analyst should be careful to ensure that the sample is thoroughly homogenized before subsampling.

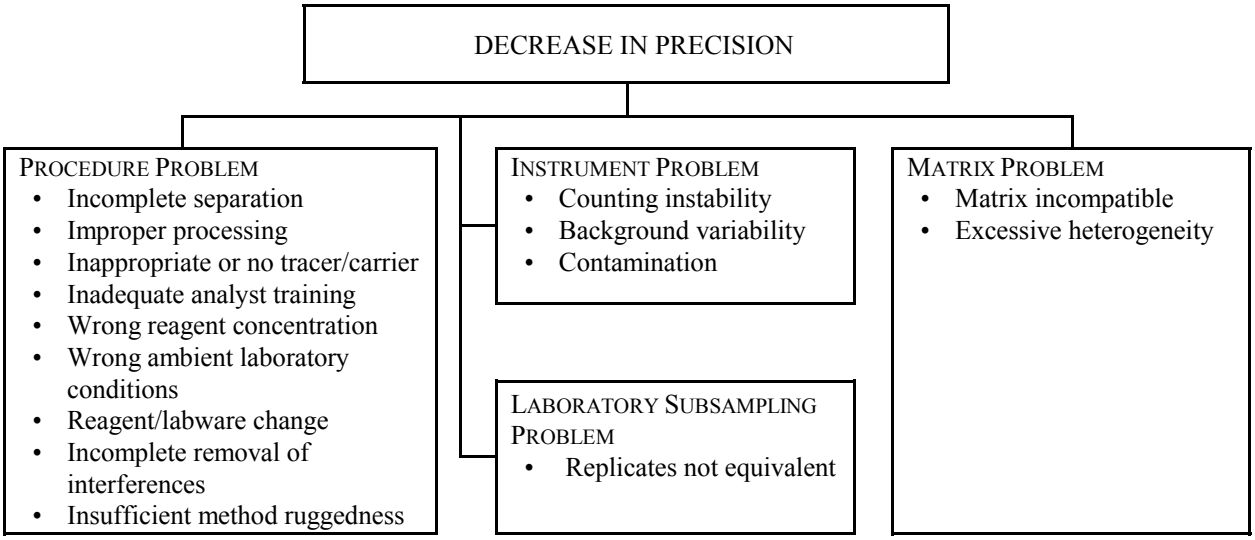

FIGURE 18.4 — Failed performance indicator: replicates

- Matrix – Sample constituents interfere with preparation chemistry, e.g., coprecipitation of interfering nontarget radionuclides from sample or excessive dissolved solids.

- Counting statistics – Sample activity is so low that small statistical variations in background

cause disproportionate responses.

- Contamination – Intermittent contamination from measurements system, glassware, etc., produces anomalous data for the original sample, but not the duplicate/replicate.

- Other – Failed chemical process, failed instrumentation, training, failed lab environment, failed procurement control.

18.4.3 Laboratory Control Samples, Matrix Spikes, and Matrix Spike Duplicates

Issue: A laboratory control sample (LCS) is a QC sample of known composition (reference material) or an artificial sample, created by fortifying a clean material similar in nature to the environmental sample. The LCS is prepared and analyzed in the same manner as the environmental sample. A matrix spike is typically an aliquant of a sample fortified (spiked) with known quantities of target radionuclides and subjected to the entire analytical procedure to establish if the method or procedure is appropriate for the analysis of a particular matrix. In some cases, specifically prepared samples of characterized materials that contain or are spiked with the target radionuclide and are consistent with the sample matrix may be used as matrix spikes. Matrix spikes should be used for those methods that do not include a radiotracer or internal carrier in the chemical separation process and where there is sufficient sample. A matrix spike duplicate (MSD) is a second-replicate matrix spike that is used to evaluate the method precision. Matrix spike duplicates are used in a similar fashion as laboratory sample replicates, but in cases where there are insufficient quantities of target radionuclides in the laboratory sample replicates to provide statistically meaningful results.

An important performance indicator is the ability to ensure that the analytical methods employed obtain data that are representative of the true activity in a sample, i.e., produce data that are accurate. The routine analysis of spiked samples provide data for an evaluation of the laboratory's reported measurement uncertainty and allow for the determination of bias, if one exists. Evaluation is typically performed using prepared samples consisting of media equivalent to a routine analytical sample with a known, measurable amount of the analyte of interest. Upon completion of the analysis, the results are compared to the known or accepted value, and the agreement is evaluated using a predetermined criterion. The range of sample types assayed in a laboratory may require the preparation of spikes using several sample media. Use of matrix spiked samples will reflect the analytical method's ability to make accurate quantitative determinations in the presence of the matrix.

Discussion: As stated previously, analytical samples cover a range of physical forms or matrices, and each matrix can change a method's expected accuracy. Tracking sets of LCS and matrix spike results can give laboratory personnel an indication of the magnitude of an observed method bias. Care must be taken when analyzing site specific matrix spike results because these matrices

may be very complex and subject to large variability. In general, the variability of matrix spikes in aqueous samples tends to be less affected than other media like soils or heterogeneous mixtures. However, multi-phase or high-solid-content fluids and brackish or saline waters may be more problematic.

The analyst should carefully consider the spiking levels for laboratory control samples and matrix spikes. Spikes and LCSs may be prepared near the lower limits of detection to test the method's performance on clean samples or samples containing small quantities of the target analytes. Conversely, matrix spikes and LCSs may be spiked at high levels for samples having high concentrations of target analytes. The laboratory should try to spike at or near the action level or level of interest for the project.

Examples of numerical performance indicators for laboratory control samples and matrix spikes are

$$Z_{\mathrm{LCS}} = \frac{x - d}{\sqrt{u_c^2(x) + u_c^2(d)}} \tag{18.3}$$

$$Z_{\mathrm{MS}} = \frac{x - x_0 - d}{\sqrt{u_c^2(x) + u_c^2(x_0) + u_c^2(d)}} \tag{18.4}$$

where x is the measured value of the spiked sample, d is the spike concentration added, x_0 is the measured concentration of the unspiked sample, and $u_c^2(x)$, $u_c^2(d)$, and $u_c^2(x_0)$ are the squares of the respective standard uncertainties. The warning limits for either of these indicators are ±2 and the control limits are ±3.

Excursions: Excursions in the LCSs and MSs can be used to identify various out of control situations. The advantage to the LCS is that the sample matrix is always the same so matrix effects should not be a factor in evaluating excursions. A rapid and one-time excursion in the LCS usually indicates that a mistake was made in the procedure. A rapid change with continued occurrences suggest that something occurred that is out of the ordinary, such as a new analyst performing the procedure or a new standard solution or new reagents being used. If an LCS shows elevated concentrations, analysts should check for contamination sources or poorly prepared spiking solutions. Slow changes showing a trend usually indicate degradation or contamination of equipment or reagents and may be indicative of bias and should be investigated.

Excursions of MSs can be difficult to interpret if the matrix changes from batch to batch. However, an excursion may indicate that the method is not appropriate for a particular matrix. If the MS shows lower than expected concentrations, the analyst should check for poor techniques or expired or poorly prepared reagents and spiking solutions. When the chemical yield of a

process is determined through a stable isotopic carrier, lower-than-expected analyte concentrations may result from inherent quantities of the stable isotope in the sample matrix.

Elevated or depressed results for site-specific MSs need to be interpreted in conjunction with the results from LCSs. If both the LCS and site-specific MS results are elevated or depressed then the cause is usually internal to the laboratory. If only the site-specific MS is depressed or elevated, the cause usually is due to the matrix.

18.4.4 Certified Reference Materials

Issue: Certified reference materials (CRMs) are well-characterized, stable, homogeneous materials with physical or chemical properties that are known within specified uncertainty limits. Laboratories that analyze CRMs can compare their performance to the certified concentration and uncertainty levels. CRMs are used for the calibration of an apparatus or the assessment of a measurement method.

Discussion: Metrology organizations issue CRMs in various matrices with critically evaluated concentration values for the radionuclide constituents. A CRM issued by NIST or under license from NIST is called a "standard reference material" (SRM). The usefulness of a reference material depends on the characterization of the radionuclide source, activity levels, and their estimated uncertainties.

CRMs can be used as internal laboratory QC samples to evaluate the ability of analytical methods to handle the matrix. CRMs need not be known to the analyst but can be introduced into the analytical stream as a blind. Comparison of analytical results of CRMs to their certified values provides linkage to the NIST radioactivity primary standards and a measure of method accuracy.

The planning that goes into the preparation of a CRM involves the selection of analytical techniques that have adequate sensitivity and precision for specific analyses. It has become increasingly important to have available well-characterized CRMs of a natural "matrix" type, which may be used in laboratory tests of measurements of environmental radioactivity. Such materials may be used in the evaluation of competing analytical methods, and also in the cross-comparison of interlaboratory data—both at the national level and the international level.

The Ionizing Radiation Division of NIST has constructed several SRMs for radiation measurements. These are included in the 4350 series and can be ordered through NIST. One widely used SRM is the natural matrix ocean sediment (4357). The radionuclides in the NIST natural matrix SRMs are not spiked into the matrix but are incorporated through natural processes to present the analyst with the combination of species that may be faced on a routine basis. SRM 4357 has two sediment sources: the Chesapeake Bay (benign) and the Irish Sea ("hot").

The NIST natural matrix SRM project has certified actinides, fission and activation radionuclides in soils, freshwater lake and river sediments, human tissues, and ocean sediment, and is working on additional unique matrices: ashed bone, ocean shellfish, and Rocky Flats Soil-II.

A numerical performance indicator for the analysis of a CRM is essentially the same as that for a laboratory control sample. An example is

$$Z_{\mathrm{CRM}} = \frac{x - d}{\sqrt{u_c^2(x) + u_c^2(d)}} \tag{18.5}$$

where x is the measured value, d is the certified value, and $u_c^2(x)$ and $u_c^2(d)$ are the squares of the respective combined standard uncertainties. Warning limits for Z_{CRM} are ±2 and control limits are ±3.

Excursions: Excursions in the CRM results can be used to identify various out-of-control situations. The advantage of the CRM is that the sample matrix is always the same, and the levels of analytes are known to a high degree, so uncertainties in matrix effects and radionuclide content should not be a factor in evaluating excursions. A rapid and one-time excursion in the SRM usually indicates that a mistake was made in the procedure. A rapid change with continued occurrences suggest that something occurred that is out of the ordinary, such as a new analyst performing the procedure or the use of a new batch of calibration solutions or reagents. Slow changes showing a trend usually indicate degradation or contamination of equipment or reagents.

If a CRM result shows elevated concentrations, analysts should check for contamination sources or poor instrument or tracer calibration. If the results show decreased concentrations, the analyst should check for poor techniques or expired or poorly prepared reagents and solutions.

CRM results may indicate a bias in the measurement process. Tracking the performance of several consecutive CRM measurements will show if the method or the laboratory consistently obtains high or low results. If the results are consistently higher or lower than the certified values, they should be evaluated for a statistical difference, e.g., *t*-tested. When the test indicates a statistical difference, a bias is indicated and the laboratory should investigate the cause of the bias and correct or characterize it.

Example: The NIST ocean sediment SRM 4357 offers a good example of a material for evaluating a laboratory performance using a specific analytical method. The blended sediment sample has been analyzed by a number of laboratories, and 10 radionuclides have certified activity values (Lin et al., 2001). The six "natural" radionuclides concentrations tended to have normal distributions (Table 18.1a), while the four "man-made" radionuclides tended to have Weibull distributions (Table 18.1b). There are also 11 other radionuclides where the activity concentrations are not certified at this time but may be at some future time (Table 18.1c).

TABLE 18.1a — Certified Massic activities for natural radionuclides with a normal distribution of measurement results

Radionuclide	Mean ± $2s_m$ * (mBq/g)	Tolerance Limit (2.5 to 97.5%) (mBq/g)	Number of Assays
^{40}K	225 ± 5	190 – 259	31
^{226}Ra	12.7 ± 0.4	10.3 – 15.0	21
^{228}Ra	13.3 ± 0.8	9.2 – 17.4	20
^{228}Th	12.1 ± 0.3	9.7 – 14.6	40
^{230}Th	12.0 ± 0.5	9.6 – 14.4	18
^{232}Th	13.0 ± 0.3	11.6 – 14.3	18

Table 18.1b — Certified Massic activities for anthropogenic radionuclides with a Weibull distribution of measurement results

Radionuclide	Mean ± $2s_m$ * (mBq/g)	Tolerance Limit (2.5 to 97.5%) (mBq/g)	Number of Assays
^{90}Sr	4.4 ± 0.3	2.1 – 8.4	49
^{137}Cs	12.7 ± 0.2	10.8 – 15.9	76
^{238}Pu	2.29 ± 0.05	1.96 – 2.98	65
^{239}Pu + ^{240}Pu	10.4 ± 0.2	9.3 – 13.2	84

Table 18.1c — Uncertified Massic activities. Radionuclides for which there are insufficient data or for which discrepant data sets were obtained. Uncertainties are not provided because no meaningful estimates could be made.

Radionuclide	Mean (mBq/g)	Range of Reported Results (mBq/g)	Number of Assays
^{129}I	0.009	0.006 – 0.012	6
^{155}Eu	1.4	1.2 – 1.5	2
^{210}Po	14	12 – 15	5
^{210}Pb	24	14 – 35	19
^{212}Pb	14	13 – 14	5
^{214}Bi	15	9 – 20	5
^{234}U	12	9 – 15	68
^{235}U	0.6	0.1 – 1.4	63
^{237}Np	0.007	0.004 – 0.009	9
^{238}U	12	7 – 16	76
^{241}Am	10	7 – 18	97

SRM 4357. Data for these radionuclides are provided for information only. The Massic activities are not certified at this time, but they may be certified in the future if additional data become available.

* S_m = standard uncertainty of the mean.

18.4.5 Chemical/Tracer Yield

Issue: Some methods require that radionuclides should be separated chemically from their sample matrix and purified before measurement. During chemical processing, some of the analyte radionuclide will be lost due to sample spillage, evaporation, incomplete chemical reactions (i.e., precipitation or extraction), etc., as discussed in Chapter 12. While these losses may correlate with a group of samples of similar chemical composition or from the same sampling area, they can be sample specific. For quantitative analysis, it is necessary to correct observed instrument responses for these losses for each analytical sample. Corrections are made using compounds that are stable (carriers) or radioactive (tracers). An inappropriate method for determining chemical yield may result in an analytical bias.

Discussion: Most alpha- and beta-emitting radionuclides require chemical separation prior to measurement, in part because of the short effective range of the radiation.

CARRIERS. Since it is impossible to determine exactly how much of the analyte is lost during processing, and because the physical mass of the radionuclide is too small to measure gravimetrically, a compound is added to the sample at the start of the chemical processing, and is carried through the analytical process and assayed. The added compound typically is stable and exhibits the same chemical properties as the analyte and therefore "carries" the analyte radionuclide—for example, stable barium that carries radium isotopes, or stable yttrium that carries ^{90}Y. These added compounds are called "carriers" and are added in sufficient quantity to allow gravimetric assay upon completion of the analysis. The ratio of the carrier recovered to the amount added is the chemical recovery, or yield. Because the carrier and analyte exhibit similar chemical behavior, the chemical yield of both should be equal, i.e., if 85 percent of the stable barium is recovered, then it follows that the observed instrument response represents 85 percent of the radium present in the sample.

TRACERS. For radionuclides above atomic number 83, stable isotopes do not exist, and a different approach often is taken to determine the analyte's yield. For these radionuclides, an isotope other that those being measured is added to the sample in the same manner as described above, e.g., ^{232}U used as a tracer for isotopic uranium (^{234}U, ^{235}U, and ^{238}U), ^{236}Pu, or ^{242}Pu used as a tracer for isotopic plutonium (^{238}Pu, ^{239}Pu, and ^{240}Pu).

This approach to chemical yield determination is based on the following assumptions regarding the carrier/tracer:

- It exhibits similar chemical behavior as the analyte under the protocol's conditions.
- The energy emission of the tracer and progeny should not interfere with the resolution of the analytes of interest.

- It is chemically and physically equilibrated with the sample before losses of either occur.
- Indigenous concentrations of carrier or tracer are insignificant, or are well known and can be quantified and corrected for during subsequent data analysis.
- The chemical form of carrier or tracer precipitates are consistent with what was used during the material's preparation and standardization.

Care should be taken during the analytical procedure to ensure that these assumptions are valid. Different conditions, such as a lack of equilibrium between the tracer and sample analyte, can result in inaccurate data. If there is indigenous tracer or carrier in the sample, this quantity should be known so that the appropriate correction can be made for its contribution to the chemical yield. In some cases, this will prevent the procedure's use, as described below. As stated previously, the quantity of tracer or carrier added to the sample should overwhelm its indigenous concentration, which cannot be determined for samples with unknown tracer or carrier content. A separate analysis for trace elements or interfering radionuclides could provide information to estimate the uncertainty contributed by the sample's indigenous tracer or carrier.

It should be noted that some analytical methods exclude direct assessment of the procedure's chemical yield for each sample analysis. In such cases, chemical yield typically recovery is addressed by analyzing a group of prepared standards by the same protocol and the results are analyzed statistically to derive a chemical yield factor. The recovery factor is applied to routine samples based on the assumption that the standards used for its derivation are representative of routine samples. This approach precludes the empirical assessment of a sample specific chemical yield, and would probably require scrutiny and periodic verification.

Acceptance limits for chemical/tracer yields should be specified in the laboratory's quality manual. While it is customary to establish lower limits for chemical yield, upper limits may also be necessary since excessive yields indicate a loss of analytical control. All limits developed by the laboratory should be either statistically based or based on historical data, and should include warning and control limits. The inherent differences among sample matrices generally require the use of matrix specific criteria, i.e., finished drinking water limits may differ from limits for high solid content waters, sandy soils or heterogeneous media. Irrespective of medium, where practical, the chemical yield and its uncertainty should be determined, recorded and tracked for each radiochemical measurement.

Excursions: There are several possible reasons for the yield to be outside of the acceptance limits. These are summarized in Figure 18.5 and discussed below.

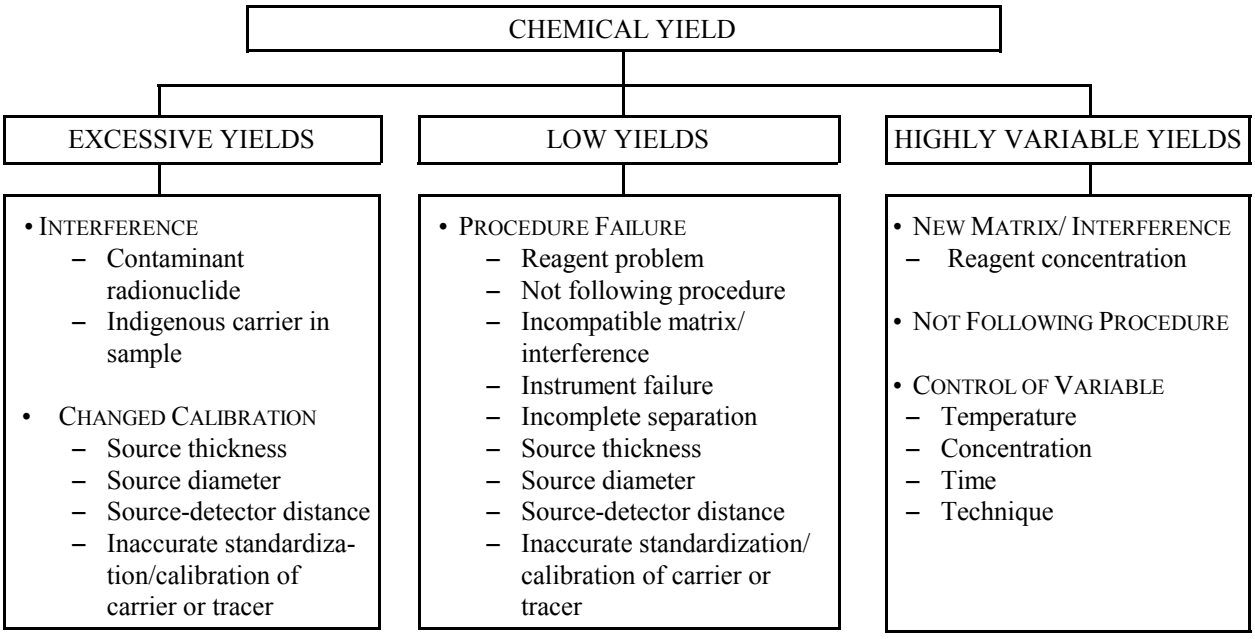

FIGURE 18.5 — Failed performance indicator: chemical yield

EXCESSIVE YIELDS: A chemical yield significantly greater than 100 percent indicates a problem. Typical causes of excessive chemical yields are provided below:

- Interference. The sample may contain an interfering radionuclide that cannot be distinguished from the tracer and therefore biases the tracer response; the sample may contain an indigenous concentration of the tracer or carrier used; or large amounts of another stable element are present.

- Counting. Changes in instrument calibration factor or other factors that affect counting, e.g., source thickness, diameter, source-detector distance or change in chemical form of final sample precipitate.

- Instrument failure.

LOW YIELDS: A very low yield usually indicates a procedural failure caused by incomplete or unsuccessful chemical separation, matrix interference, missing reagents, or the exclusion of a key element in the sample processing. A significantly lower yield will increase the overall measurement uncertainty and degrade the procedure's effective detection capability unless the counting time is appropriately extended, which may be impractical or even ineffective in many cases. Furthermore, measurement of the recovered carrier or tracer becomes increasingly more adversely affected by background, stable element, water absorption, and other corrections as the yield decreases. Fixed lower limits for yields often are established and

should be specific to analytical procedures and sample matrices. Setting an upper limit is recommended for the acceptable relative uncertainty in a yield measurement.

HIGHLY VARIABLE YIELDS: High variability in procedural temperature, concentration, time, reagent concentration, or laboratory technique can have dramatic effects on yield. Highly variable yields indicate a lack of procedural control and should be investigated and corrected. A simple step such as heating samples on a hotplate can lead to variability in yield because the hotplate surface is thermally uneven. Samples can be dried and reconstituted several times during the course of the preparation protocol, and samples may require different amounts of heat or water, which introduces additional variability. When highly variable chemical yields are observed, a careful examination of the analytical procedure's application is recommended to determine critical variables and the controls needed to re-establish adequate management over yields.

18.5 Instrumentation Performance Indicators

Radiometric and non-radiometric instruments are used currently to quantify radionuclides in a variety of environmental matrices, and quality control measures are necessary to ensure proper instrument performance. This section presents radiometric instrument performance measures that indicate a measurement system is in control. For detailed information on instrument concepts and specific techniques, see Chapter 15 as well as ASTM standard practices (e.g., D3648, for the Measurement of Radioactivity). The specific quality control procedures to be followed depend on the measurement equipment. Sufficient checks are needed to demonstrate that the measurement equipment is properly calibrated, the appropriate background has been recorded, and that all system components are functioning properly. QC measures for instrumentation should include at a minimum: (1) instrument background measurements, (2) instrument calibration with reference standards, and (3) periodic instrument performance checks subsequent to the calibration. Acceptable control limits should be specified in appropriate laboratory documents.

18.5.1 Instrument Background Measurements

Issue: In general, radionuclide detection covers more than 17 orders of magnitude of sample activity, from irradiated material that produces high radiation fields to environmental samples. All radiation detection instruments have a background response even in the absence of a sample or radionuclide source. To determine the instrument's response to the radioactivity contributed by the sample alone (net), the instrument background response is subtracted from the sample-plus-background response (gross). Background corrections become more critical when the instrument net response is small relative to the background. Careful control of contamination and routine monitoring of instrument background are therefore integral parts of a control program. Inappropriate background correction results in analytical error and will increase the uncertainty of data interpretation.

Discussion: Every radionuclide detector produces a signal response in the absence of a sample or radionuclide source. These signals are produced by electronic dark current, cosmic radiation, impurities in the instrument construction materials, crosstalk between the detector's alpha and beta channels, sources in the general vicinity of the detector, and residual contamination from previous counting episodes. The majority of these contributors (i.e., dark current, cosmic radiation, construction material impurities) to instrument background produce a fairly constant count rate, given sufficient measurement time. For other sources, instrument backgrounds vary as a function of time (i.e., from decay or ingrowth of residual contamination or as radon levels fluctuate throughout the day and season). For low-level measurements, it is imperative that the background be maintained as low as feasible. Active or passive detector shielding, removing or adequately shielding radioactive sources in the vicinity of the detector, and good laboratory practices to prevent residual contamination are necessary to maintain low instrument background.

The instrument's background should be determined in the absence of a radionuclide source. The instrument background should be well characterized. The instrument background is an important factor in determining the ability to achieve a specific minimum detectable concentration (MDC). Control limits for the background should be specified in appropriate laboratory documents. The background population considered in the statistical calculations should cover a sufficient period of time to detect gradual shifts in the measurement system's background contamination or detector instability. Additionally, backgrounds should be determined in such a way that they mimic actual sample measurement conditions as closely as possible, i.e., using appropriate sample containers, geometries, and counting times.

Background measurements should be made on a regular basis and monitored using control charts. For instruments with well established background performance records and a low probability of detector contamination, this frequency may be modified by the laboratory. For mass spectrometry and kinetic phosphorimetry analysis, background measurements should be performed on a real time basis. See ASTM E181, ANSI N42.12, and NELAC (2002) *Quality Systems Appendix D* for more information on the suggested frequency of background measurement.

Excursions: Variations in instrument backgrounds may indicate instrument malfunction. Variations may take the form of rapid increase or decrease in background, slow increase or decrease in backgrounds, and highly variable or erratic backgrounds. These variations can result in the measurement system's reduced precision and decreased detection capability. Rapid or significant increases in background measurements may be due to instrument or blank contamination, insufficient shielding with relocation of nearby radionuclide sources, or large scale equipment malfunction (e.g., a broken window on a gas proportional system).

Instrument background data should be evaluated for trends, which is facilitated by regular inspection of control charts. A slowly changing background could alert laboratory personnel to a potentially serious instrument failure. A sufficient number of data points (Chapter 15) taken over

time should be included in any trend analysis. Slowly changing instrument backgrounds could be caused by low counting-gas flow rates, small incremental instrument contamination, or electronic drift or noise.

When the instrument background is more variable than expected, the reliability of measurements becomes questionable, resulting in loss of confidence and increased uncertainty. This indicates a loss of control over the measurement environment, or limitations of the data handling software. The root cause of the variability should be identified and corrected to re-establish statistical control over the instrument background. Table 18.2 presents reasons for changing backgrounds.

TABLE 18.2 — Instrument background evaluation

Instrument Background Failed Performance Indicator		
Rapid Change in Background	**Slow Change in Background**	**Excessively Variable Background**
Electronic failure Detector failure Loss of coolant/vacuum Instrument contamination Counting gas changes Temperature/humidity fluctuation Laboratory contamination External sources Insufficient shielding Personnel with nuclear medicine dose	Instrument contamination Electronic drift Low counting gas flow rate	Sources being moved Radon fluctuation Insufficient shielding Insufficient counting statistics Interfering radionuclides Poor peak deconvolution Intermittent electrical grounding problems Failing electronics

18.5.2 Efficiency Calibrations

Issue: This section discusses selected aspects of instrument calibration that are pertinent to laboratory quality control. A more in-depth, technical discussion is provided in Chapter 16. The number of events (counts) recorded by a detector is converted to activity (actual radionuclide transformations) by empirically determining this relationship with NIST-traceable radionuclide sources when available. This relationship is expressed in the system's efficiency calibration. A separate efficiency is determined for each detector-source combination and is typically energy or radionuclide specific.

Detector efficiency is critical for converting the detector's response to activity. As discussed above, routine performance checks can evaluate several aspects simultaneously (sample geometry, matrix, etc.) and provide a means to demonstrate that the system's operational parameters are within acceptable limits. These are typically included in the assessment of the analytical method's bias and are specified in terms of percent recovery based on the source's known disintegration rate. Performance checks for measurement efficiency are usually determined statistically from repeated measurements with a specific check source. Detection of a shift in measurement efficiency should be investigated.

The frequency of performance checks for efficiency calibrations is instrument specific. The frequency of these checks is often based on a standardized time scale or a percentage of the total number of analyses performed using that method.

Performance checks for instrument efficiency typically are performed on a day-of-use basis. The level of activity in the check source should be sufficient to allow the accumulation of enough counts in a short time so that daily performance checks do not impose an unnecessary burden on the laboratory. However, the source strength for spectrometry systems should be such that instrument dead time is not significant and gain shifts do not occur (ANSI 42.23). For detectors that are used infrequently, it may be necessary to perform a check before and after each set of measurements.

Control charts provide a useful tool for documenting and evaluating performance checks for efficiency calibrations, and should be established and maintained for the intrinsic efficiency of each detector. There are several methods available for evaluating performance using control charts (see Attachment 18A).

Discussion: Most radiation detectors do not record all of the nuclear transformations that occur in samples undergoing measurement, i.e., they are not one hundred percent efficient. This occurs for several reasons, and the prominent reasons are discussed briefly below.

- Intrinsic or absolute efficiency[2] – In the absence of all other factors, a detector will only record a fraction of the emissions to which it is exposed due to its composition and other material-related aspects. Intrinsic efficiency is a measure of the probability that a count will be recorded when a particle or photon of ionizing radiation is incident on a detector (ANSI N1.1).

- Geometry – The spatial arrangement of source, shielding, and detection equipment, including the solid angle subtended by the detector and sample configuration, largely determines what fraction of the emissions from the source actually reach the detector (ANSI N15.37). Geometry includes the source's distance from the detector and its spatial distribution within the counting container relative to the detector and shielding components.

- Absorption – Radiation emitted by the source can be absorbed by the source itself (self-absorption), as well as other materials placed between the source and the detector, i.e., source container, detector housing, and shielding (NCRP 58).

[2] Efficiency measures the fraction of emitted photons or particles that are actually detected. It is affected by the shape, size, and composition of the detector as well as by the sample-to-detector geometry. There are two ways that efficiency can be expressed: "Absolute efficiency" is the fraction of all the photons or particles emitted by the source that are actually detected, and "intrinsic efficiency" is the ratio of photons or particles detected to the number that actually fall on the detector.

- Backscatter – Radiation emitted by the source can hit the source container or detector shielding and scatter into the detector.

The detector response is a composite of these factors.

Each radiation detector should be calibrated to determine the relationship between the observed count rate of the detector and the emission rate of the source being assayed. This relationship is called the efficiency calibration—typically expressed in counts per second/emissions per second, or cps/dps—and is an integral part of the measurement protocol. For alpha spectrometry systems, the efficiency of detection is energy-independent. Efficiencies for gamma spectrometry are energy dependent, and an efficiency calibration typically covers a range for a specific counting geometry, e.g., 50 to 1,800 keV.

Once this relationship is established, it should be checked at regular intervals using what is called a performance or calibration check. The performance check does not seek to reestablish the detector's efficiency but simply demonstrates that the relationship is within acceptance limits. When designed properly, an efficiency performance check evaluates the intrinsic efficiency, geometry and absorption in a single measurement. Accordingly, it takes the form of a single value that incorporates all effects for a target radionuclide and a specific detector-sample configuration. Detectors that are energy dependent and measure radionuclides with multiple energies, such as photon or alpha spectrometers, should have performance checks at several energies throughout the measurement range. For these detectors, the performance check can simultaneously address the system's efficiency, energy calibration and resolution using a single source. An internal pulser can be used to check the electronics.

Because the performance check's purpose is to demonstrate that the system's efficiency remains constant, the source's absolute disintegration rate need not be known, provided its purity can be established, its half-life is known, and its activity is sufficient to provide adequate precision. Accordingly, it is not necessary to use a NIST-traceable check source for this purpose. Check sources that are non-NIST-traceable can meet the precision objectives of the performance check and they are less expensive.

Excursions: Changes in the efficiency of a detector can only be corrected by determining the root cause of the problem and repeating the efficiency calibration. Gradual changes in geometry usually indicate a problem with the technique of sample mounting or preparation. A visual inspection of the prepared source is often helpful in eliminating sample geometry as a cause of the problem. For example, a precipitated sample counted on a gas proportional counter has an expected appearance, i.e., a circle of precipitate centered on the planchet and often covered with thin plastic film. If the prepared source does not have the correct appearance, there could be a problem with the geometry, self-absorption, and backscatter. This can sometimes be corrected by

preparing the source a second time, inspecting it and presenting it for counting a second time. Re-training personnel responsible for the error may also be indicated. Because sources that have been improperly prepared for counting can result in contamination of or physical damage to the detector, it is strongly recommended that every source be visually inspected prior to counting. Significant changes in geometry caused by modifications to the source preparation method can only be corrected by recalibrating the detector. Examples of modifications to source preparation methods are (1) using a new filter so that the geometry of the test source is different than the geometry used for calibration, and (2) replacing the containers used for gamma spectrometry with containers that have a different wall thickness or are made from different materials.

Changes in intrinsic efficiency generally result from a physical change to the detector and often result in rapid changes in efficiency. In many cases, changes that affect the intrinsic efficiency of a detector render it inoperable. These are specific to a detector type and are listed below:

- HPGe, Ge(Li), and surface barrier detectors – Real or apparent changes in intrinsic efficiency may be caused by vacuum leaks or failure of field effect transistor.

- Thin window detectors (gas proportional counters, low-energy photon) – Changes in measurement efficiency are typically associated with damage to the detector window.

- Gas proportional systems – Problems may be related to the quality or flow of counting gas.

- Anti-coincidence systems with guard detectors – Electrical problems with the anti-coincidence circuits may produce apparent changes in efficiency.

- Scintillation detectors – Gradual changes in efficiency are associated with the scintillator or the photomultiplier tube. For example, NaI(Tl) crystals may gradually turn yellow over time resulting in a lower intrinsic efficiency, and liquid scintillation counters may have residue gradually build up on the surface of the photomultiplier tube affecting the detection of photons by the tube.

18.5.3 Spectrometry Systems

18.5.3.1 Energy Calibrations

Issue: This section discusses selected aspects of instrument calibration that are pertinent to laboratory quality control. A more in depth, technical discussion of instrument calibration is provided in Chapter 15 (*Quantification of Radionuclides*). All radiation measurements are energy dependent to a certain extent. However, spectrometric techniques such as gamma and alpha spectrometry identify radionuclides based on the energy of the detected radiations. For these techniques a correct energy calibration is critical to accurately identify radionuclides. Problems

with energy calibration may result in misidentification of peaks.

Discussion: Spectrometry systems should be calibrated so that each channel number is correlated with a specific energy. To identify radionuclides correctly, this energy calibration needs to be established initially and verified at regular intervals. The energy calibration is established by determining the channel number of the centroid of several peaks of known energy over the applicable energy range. Typically, a minimum of three peaks is used, and commercially available sources contain nine or ten photopeaks. The relationship between energy and channel number can be determined by a least squares fit. To account for non-linearity, a second or third order fit may be used. However, these require more points to define the curve. For example, a first order calibration requires at least two points, while a second order calibration requires a minimum of three points. The end points of the curve define a range of applicability over which the calibration is valid, and peaks identified outside the curve's range should be used carefully. The uncertainty associated with the curve should be available at any point along the calibration curve.

Quality control checks for energy calibration may be combined with checks for efficiency calibration and resolution. Radiations emitted over the range of energy of interest are measured, and two or more peaks are used to demonstrate that the energy calibration falls within acceptable limits. Check sources may consist of a single radionuclide or a mixture of radionuclides (e.g., mixed gamma). Because only the location of the peak is of concern, there is no requirement that the check source be calibrated or certified, except for ensuring that it does contain the radionuclide(s) of interest at a specified level of purity.

The energy calibration is determined when the system is initially set up by adjusting the gain of the amplifier, analog-to-digital conversion (ADC) gain, and zero. Criteria that indicate when readjustment is required because of gradual and abrupt changes in the energy versus channel calibration should be established as an integral part of the system's operating procedure. These changes usually are monitored by the measurement system's software, and the user specifies the allowable difference between that the system's response and the radionuclide's known energy. The tolerable difference often relates to the instrument's resolution. For example, a high resolution instrument such as an intrinsic germanium detector typically will have acceptable limits on the order of a few keV, while a low resolution instrument such as a NaI(Tl) detector typically will have acceptable limits on the order of several tens of keV.

Spectra also can be analyzed by identifying each peak manually. With manual identification, the acceptable limits for the energy calibration are determined for each spectrum based on the professional judgment of the person analyzing the spectrum.

The frequency of QC checks for energy calibrations can be related to the expected resolution of the instrument, the electronic stability of the equipment, or the frequency needs of QC

measurements for efficiency calibration or resolution. These are specified typically in the laboratory's quality manual or other typical project-related documentation. Examples for three detector types are provided below and in Tables 18.5 through 18.8.

- HPGe and Ge(Li) Photon Detectors. Energy calibrations are typically verified using a check source on a day of use basis. Every source spectrum should include verification of the energy calibration as part of the data review process, when possible. Under extreme conditions (e.g., *in situ* measurements in bad weather), it may be necessary to perform checks at the beginning and end of each measurement period or day the instrument is used.

- Surface Barrier Alpha Spectrometry Detectors. The energy calibration is often performed using an alpha source when the instrument is setup initially and when a detector has been serviced or replaced. Electronic pulsers can be used for daily checks on energy calibration. Most alpha spectra include a chemical yield tracer with a peak of known energy that can be used to verify the energy calibration during data review. Alpha spectrometers have a lower resolution than germanium detectors, and newer spectrometers are sufficiently stable to allow weekly or monthly performance checks. The frequency of performance checks should be based on the number and frequency of measurements and historical information on the stability of the instrument.

- Low-Resolution NaI(Tl) Detectors. These typically are less stable than HPGe detectors and may require more frequent quality control checks, depending on the conditions under which they are used.

For all detectors where energy calibrations are performed daily, plotting the channel numbers of peak centroids can be useful for identifying trends and determining the need for adjusting the system. Changes in peak location may result in mis-identification of radionuclides. When this is observed, all spectra obtained since the last acceptable energy calibration check should be reviewed. If there is sufficient information within the spectrum to determine the acceptability of the energy calibration, no further action may be required for that spectrum. If the spectrum contains too few peaks of known energy, reanalysis should be initiated.

Gradual changes in peak location are not unexpected and the rate of these gradual changes can be used to establish the appropriate frequency of energy calibration checks. The acceptable limits on peak location established during the initial system setup may be used to indicate when the energy calibration needs to be readjusted.

Excursions: Changes in the energy calibration can be the result of many factors including power surges, power spikes, changes in the quality of the electrical supply, variations in ambient conditions (e.g., temperature, humidity), physical shock to the detector or associated electronics, and electronic malfunction.

Rapid changes in energy calibration are usually caused by power surges, power spikes, or physical shocks to the system. Corrective actions typically involve recalibrating the system and repeating the analysis. If changes result due to loss of cryostat vacuum, the instrument may need to be returned to the manufacturer to be refurbished or replaced.

Gradual changes in the energy calibration are usually the result of a variable or poorly conditioned power source, changes in the ambient conditions, or electronic malfunction. Corrective actions generally begin with identifying the root cause of the problem. Gradual changes that begin following relocation of the instrument are more likely to be caused by the power source or the ambient conditions. Installing a line conditioner, surge protector, and uninterrupted power supply is recommended to address problems related to the system's electrical power source. Problems with low humidity can be corrected through the use of a humidifier in dry climates or cold weather; conversely, high or variable humidity may require the use of a dehumidifier. Problems associated with fluctuations in temperature may require significant changes to the heating and cooling system for the room or building containing the instrument in order to stabilize the temperature. Gradual changes that occur following physical shocks to the system or following a rapid change in peak location with an unidentified cause are more likely to be the result of problems with the electronic equipment. In most cases the amplifier is the source of these problems, but the analog-to-digital converter, pre-amplifier, power supply voltages, and multi-channel (or single-channel) analyzer may also cause this type of problem. However, they could also be the result of crystal or detector failure. Systematic switching out of components and discussions with the instrument manufacturer will often help to identify which component may be the source of the trouble. It may be especially difficult to identify the source of problems with new instruments in a new facility.

18.5.3.2 Peak Resolution and Tailing

Issue: The shape of the full energy peak is important for identifying radionuclides and quantifying their activity with spectrometry systems. Poor peak resolution and peak tailing may result in larger measurement uncertainty. If consistent problems with peak resolution are persistent , then an analytical bias most likely exists. Many factors will affect peak resolution and these are discussed below.

Discussion: Detectors with good resolution permit the identification of peaks which are close in energy. When a monoenergetic source of radiation is measured with a semiconductor, scintillation, or proportional spectrometer, the observed pulse heights have a Gaussian distribution around the most probable value (Friedlander et al., 1981). The energy resolution is usually expressed in terms of the full width at half maximum (FWHM) or the full width at tenth maximum (FWTM).

In a semiconductor detector, fluctuations in output pulse height result from the sharing of energy

between ionization processes and lattice excitation (Friedlander et al., 1981). The number of charge pairs created by radiation of a given energy will fluctuate statistically. This fluctuation occurs because the energy causes lattice vibrations in the semiconductor as well as the formation of charge pairs. This sharing of energy causes a variation in the number of charge pairs created and gives rise to the width of a measured peak. The magnitude of the statistical fluctuation is proportional to the energy of the radiation. There is also a variation in the number of charge pairs collected by a detector.

In a scintillation detector, the statistical fluctuations in output pulse heights arise from several sources. The conversion of energy of ionizing radiation into photons in the scintillator, the electronic emission at the photocathode, and the electron multiplication at each dynode are all subject to statistical variations. Note that the distance of the source to the detector also impacts the resolution.

In a proportional counter, the spread in pulse heights for monoenergetic rays absorbed in the counter volume arises from statistical fluctuations in the number of ion pairs formed and the gas amplification factor (Friedlander et al., 1981). If the gas gain is made sufficiently large, the fluctuations in the number of ion pairs determine the resolution.

The FWHM typically is used as a measure of resolution, while the FWTM is used as a measure of tailing for the full energy peak. For Gaussian peaks with standard deviation σ, the FWHM is equal to 2.35σ. The resolution of a detector is the ratio of the FWHM (in keV) to the energy (in keV) at the most probable peak height. The sources of fluctuations that contribute to the standard deviation are dependent on the type of detector (see Chapter 15, *Quantification of Radionuclides*, for a more detailed discussion of detector resolution).

Resolution affects the ability to identify individual peaks in two ways (Gilmore and Hemingway,1995). First, it determines how close together two peaks may occur in energy and still be resolved into the two components. Second, for gamma spectrometry, when a peak of small magnitude sits on the Compton continuum of other peaks, its ability to be detected can depend on its signal-to-noise ratio. With good resolution, the available counts are distributed in fewer channels, thus those counts will be more easily identified as a peak by the spectrometry analysis software. If resolution degrades significantly the efficiency may be in error. This is especially true when the spectrum analysis involves the region of interest (ROI) concept. When the calibration is performed, the full energy peak may fit within the defined ROI limits, whereas the resolution degraded peak may have counts which fall outside them. Thus, the detector efficiency will be effectively decreased and inconsistent with the previously determined efficiency.

Tailing is another observable feature of the peak shape. Tailing is an increased number of counts in the channels on either side of the full energy peak. Tailing affects the FWTM more than the FWHM, so the ratio of FWTM to FWHM can be used as a measure of tailing. For a Gaussian distribution the ratio of FWTM to FWHM is 1.823. For most germanium detectors this ratio

should not exceed 2.0. Tailing may be caused by imperfect or incomplete charge collection in some regions of the detector, escape of secondary electrons from the active region of the detector, electronic noise in the amplification and processing circuitry, loss of vacuum and escape of bremsstrahlung from the active region of the detector. Tailing may also result from the source's self-absorption for alpha emitting radionuclides.

The resolution (FWHM) is routinely calculated for gamma and alpha spectrometry peaks by the spectrum analysis software and can be monitored by observing the FWHM calculated for the check sources routinely counted. Resolution monitoring and charting is normally an integral part of a measurement quality system. Acceptance parameters may be established for resolution and incorporated in the analysis software. For alpha spectrometry, where radionuclide tracers are used for chemical yield determination, the FWHM can be monitored for each analysis, if desired. Some projects may specify FWHM limits for internal tracer peaks on each sample run.

The shape of the peak is important for quantifying the activity, and resolution is important for identifying peaks in a spectrum. The shape of the peak is also important for monitoring the performance of a detector. Germanium detectors have very good resolution on the order of 1 percent. The FWHM at specific energies is provided by the manufacturer. The FWHM should be established at several energies throughout the range being measured because the FWHM is directly proportional to the energy. These energies are usually the same as those used for checking the energy calibration and the efficiency calibration. Tolerance or ontrol limits for FWHM and the ratio of FWTM to FWHM may be developed based on statistics using multiple measurements collected over time.

The resolution of an alpha spectrum is dominated typically by self-absorption in the source. This is indicated by low energy tailing and elevated FWTM and FWHM. Most surface barrier detectors are capable of resolutions on the order of 30-40 keV for monoenergetic nuclides and 80-100 keV for unresolved multiplets. Acceptance of sample resolution is usually monitored by visual inspection of individual spectra. For well-prepared samples, the FWHM of the alpha peaks may be expected to be from 30 to 80 keV.

The resolution of scintillation detectors is not as good as the resolution of semiconductor detectors, but peak shape and tailing are just as important for analyzing samples. The FWHM should be established at several energies throughout the range being measured. These energies are usually the same as those used for checking the energy calibration and the efficiency calibration. Control limits for FWHM and the ratio of FWTM to FWHM may be developed based on statistics using multiple measurements collected over time.

Performance checks for resolution and tailing should be performed for all instruments used as spectrometers. These measurements are usually combined with the performance checks for energy calibration and efficiency calibration. Quality control activities should include visual inspection of all spectra to evaluate peak shape and tailing.

Tolerance limits or control charts for FWHM and the ratio of FWTM to FWHM can be developed and used to monitor the performance of any detector used as a spectrometer. Because the concern is when the resolution degrades (i.e., the FWHM increases) or tailing becomes a problem (i.e., the ratio of FWTM to FWHM increases), control limits are necessary. Limits can be developed based on historical performance for a specific type of detector. Control charts offer a convenient method for monitoring the results of the performance checks. As mentioned previously, the concern is associated with an increase in the FWHM or the ratio of FWTM to FWHM. This means that only an upper control limit or tolerance limit is required for the chart.

Excursions: Changes to the FWHM are associated with malfunctioning or misadjusted electronics, excessive electronic noise or interference, or detector or source problems. Electronics problems include changes in the high voltage applied to the detector, noise (including cable noise and high voltage breakdown), and electronic drift. Electronics problems may be caused by changes in the high voltage, improper adjustment of the pole zero or baseline restorer, or drift of the amplifier gain or zero during acquisition. Source problems are usually only associated with alpha spectra and result in excessive self-absorption resulting in low-energy tailing. This can result in counts being identified with an incorrect peak. Problems that are not electronic or source related imply that the detector is malfunctioning.

Changes to the ratio of FWTM to FWHM indicate problems associated with tailing. Tailing can occur on the high- or low-energy side of the peak. High-energy tailing indicates electronics problems that may be caused by excessive activity in the sample, incorrect adjustment of the pole zero or pile-up rejector, or drift of the amplifier gain or zero while acquiring the spectrum. Low-energy tailing indicates an electronic or a source problem—a possible corrective action is to check to see if the vacuum is set properly for alpha detectors. Table 18.3 lists common problems, the implied root cause of the problem, and possible corrective actions.

TABLE 18.3 — Root-cause analysis of performance check results for spectrometry systems

Observed Problem	Implied Root Cause	Possible Corrective Actions
Efficiency changed	Unknown Electronics degradation Geometry changed Poor source Software application	Ensure the correct check source was used Check to ensure the efficiency was evaluated using the correct geometry Ensure high voltage is set properly Pulser check of electronics
Peak centroid moved	Gain changed	Check amplifier gain Check conversion gain Check stability of amplifier for gain shifts or drifting
	Offset shifted	Check zero offset Check digital offset Check stability of amplifier for gain shifts or drifting
FWHM changed	Electronics problem	Ensure high voltage is set properly
	Source problem	Increased source-to-detector distance (for alpha spectrometry)

Observed Problem	Implied Root Cause	Possible Corrective Actions
FWTM changed	Electronics problem	Ensure high voltage is set properly
	Source problem	Repeat test-source/sample preparation and recount Reanalyze sample Check with weightless (plated) source Increased source-to-detector distance (for alpha spectrometry)
No peak or broad peaks	Electronics problem	Ensure that high voltage is correct
Low-energy tailing	Electronics problem	Ensure that high voltage is correct Check pole zero adjustment Check baseline restorer Check stability of amplifier for gain shifts or drifting Check for loss of vacuum
	Source problem	Repeat test-source/sample preparation and recount Reanalyze the sample
High-energy tailing	Electronics problem	Check pole zero adjustment Check pile-up rejector Check stability of amplifier for gain shifts or drifting
	Source problem (too much activity)	Reduce volume of sample analyzed Increase distance between the source and detector
Spectra shifted uniformly	Offset shifted	Check zero offset Check digital offset Check amplifier for zero drift
Spectra stretched or compressed	Gain changed	Check amplifier gain Check conversion gain Check amplifier for gain shifts

18.5.4 Gas Proportional Systems

18.5.4.1 Voltage Plateaus

Issue: The accuracy of the results produced by a gas proportional system can be affected if the system is not operated with its detector high voltage properly adjusted, such that it is on a stable portion of the operating plateau.

Discussion: The operating portion of a detector plateau is determined by counting an appropriate source at increasing increments (e.g., 50 volts) of detector high voltage. For detectors which will be used to conduct analyses for both alpha- and beta-emitting radionuclides, this should be done with both an alpha and beta source. The sources used should be similar in both geometry and energy to that of the test sources to be counted in the detector.

A plot of the source count rate (ordinate) versus high voltage (abscissa) rises from the baseline to a relatively flat plateau region, and then rises rapidly into the discharge region for both the alpha

and beta determinations. From the plateau, the operating voltage is selected so that small voltage changes will only result in minor fluctuations to detector efficiency. Operation of the counter at the upper end of the plateau is not recommended and can result in the generation of spurious discharge counts. Modern high-voltage supplies, operating properly, experience little actual voltage fluctuation. The detector response should be checked after repairs and after a change of gas. The detector plateau should again be determined and plotted (voltage vs. count rate) after repairs, particularly to the detector unit.

The historical tracking of the establishment and maintenance of this operating parameter is recommended; it aids in determining the probable cause of quality control failure and the identification of long-term instrument deterioration. Items to be recorded include date/time, instrument detector designation, source number, check source response at the operating point, and pertinent instrument parameters, such as lower level discriminator setting, alpha-discriminator setting, length of the plateau, operating high voltage setting, etc.

Excursions: Voltage changes of short- or long-term duration will affect reliability of a proportional counter. If the detector voltage is lowered sufficiently, there is a danger of operating below the plateau knee which, in effect, reduces the efficiency and would bias the results of any sample count low. Should the voltage applied to the proportional detector be driven up to a point where the slope of the plateau is sufficiently great enough to increase the efficiency of the detector, sample counts may be biased high. A transient voltage increase of great enough magnitude could introduce spurious counts.

Shifts in the operating voltage along the plateau or length of the plateau could also result from long-term detector deterioration or electronic drift or failure.

18.5.4.2 Self-Absorption, Backscatter, and Crosstalk

Issue: The accuracy of alpha and beta activity determinations in samples with discernable solids in a gas proportional system depends in large part on the determination and maintenance of self-absorption and crosstalk curves.

Discussion: Samples counted for alpha and beta activity in a gas proportional system are typically prepared as inorganic salts, e.g., nitrates, carbonates, oxides, sulfates, or oxalates, and contain on the order of tens to hundreds of milligrams of solids when counted, which result in absorption and scattering of the particles in the sample material and mounting planchet (Chapter 16). Thus, for gas proportional systems, the detection efficiency for a given test source depends on the self-absorption occurring within each sample volume/mass. To establish the correction factor, a calibration curve is generated using a series of calibration sources consisting of an increasing amount of solids and known amounts of radionuclide. The relative efficiency for each calibration source is plotted against the amount of solids, and these data are used to determine a

test source's efficiency as a function of test-source mass. The diameter and the composition of the test-source planchet, not just the test-source mass, should be identical with what was used for routine samples. This allows calculation of the corrected amount of activity regardless of the test-source mass (mass/efficiency curves).

The counting of alpha and beta particles simultaneously in a proportional counter requires that an electronic discriminator be adjusted, such that pulses of heights below that represented by the discriminator are registered as betas, and those of greater heights are counted as alphas. Crosstalk occurs when alpha particles are counted in the beta channel or betas are registered as alphas. For example, the alpha-to-beta crosstalk for ^{241}Am, which also has a 59.5 keV gamma-ray emission (35.9 percent), would be greater than the alpha-to-beta crosstalk factor for a pure alpha emitter (such as ^{210}Po). However, this relationship is energy dependent, and care should be taken to identify samples that differ significantly from the sources used to establish the crosstalk ratio. For example, ^{90}Sr + ^{90}Y ($E_{\beta max}$ 2.28 MeV) is typically used as a beta source for instrument calibration. However, samples containing natural uranium in equilibrium with its progeny produce beta emissions that are considerably more energetic from the 3.28 MeV $E_{\beta max}$ betas of ^{214}Bi. The crosstalk ratio established with ^{90}Sr will be inadequate for such samples.

As the amount of solids in the test source increases, the beta crosstalk can increase due to the degradation of the alpha particle energy by interaction with test-source material. Similarly, the beta into alpha crosstalk decreases. Thus, crosstalk should be evaluated as a function of sample weight to correct the observed relative alpha and beta counts. This is normally determined in conjunction with the self-absorption curve. To check these parameters, calibration sources should be prepared at the low and high ends of the calibration curve, and the limit of their acceptability should be better than 1 percent (one sigma). These checks should be performed annually, at a minimum, and following detector replacement or significant repair. The historical tracking of the establishment and maintenance of these operating parameters is recommended. This aids in determining the probable cause of quality control failure and the identification of long-term instrument deterioration. In addition, items to be recorded include date/time, instrument detector designation, source number, operating point, and pertinent instrument parameters, such as lower level discriminator setting, alpha discriminator setting, etc.

Excursions: Any change in the detector-source geometry or adsorption characteristics between the source and detector, can affect the self-absorption and crosstalk correction factors. For example, the replacement of a detector window with one whose density thickness is different from the original window can necessitate the reestablishment of these parameters. Electronic drift of the alpha discriminator can also affect the crosstalk ratios.

18.5.5 Liquid Scintillation

Issue: The accuracy and reproducibility of radionuclide measurements by liquid scintillation are

dependent on accounting for the quench (Section 15.5.3.3) of the measured test source. Quench is one of the most significant factors to be accounted for, and can be affected by solvent-to-fluor ratio, cocktail characteristics, suspension composition, acid concentration, and chemical and radiological impurities. Care must be taken to assure radionuclide purity and chemical-composition equivalence to calibration and test sources. An additional factor to consider is the ratio of sample volume to scintillation-cocktail volume (i.e., dilution factor). Although this can affect quench as well (especially if there is significant sample dilution), it is more critical that the ratios used for calibration match those in the test-source analysis.

Discussion: The process of scintillation involves the energy transfer from the emitted beta particles, slowing and stopping in the liquid medium as a result of collisions with molecularly bound electrons. The transfer of energy from the beta particle to the electrons results in solvent excitation through thermal, collisional, and photonic interactions. These excited solvent molecules transfer energy through various processes to specific organic molecules known as "fluors." The combination of the solvent and fluor is referred to as the "cocktail." The test source is the combination of the cocktail and sample.

Fluors absorb the energy and are brought to an excited state. The de-excitation of these molecules results in a photon emission that is detected by a photomultiplier tube. Many cocktail combinations contain a second fluor (referred to as a wavelength shifter) which adjusts the emitted photons to a specific bandwidth.

Any component of the cocktail that affects the energy transfer process will have a significant effect on the analysis. This effect is referred to as "quench." The quench of a cocktail can be affected by:

- Color;
- Turbidity;
- Molecules of high electron affinity;
- Solvent;
- Acidity; and
- Dissolved gases.

Quench has the effect of shifting the energy distribution of the beta particle spectrum to lower energies. Quench also can have the effect of reducing the number of net counts.

Excursions: Slowly changing liquid scintillation measurements of a sample may be due to the change in quench because of chemical attack on the cocktail system or to changes in instrument or ambient temperature during a long count. Rapid changes in liquid scintillation measurements include phase separation of the sample in the cocktail, sample precipitation, and light leaks into the instrument. Some causes of excursions in liquid scintillation analysis are listed in Table 18.4.

Examples: Specific examples of these types of excursions as it affects analysis can be seen in the examples below.

TABLE 18.4 — Some causes of excursions in liquid scintillation analysis

Physical Effects	Chemical Effects
Turbidity	Elevated concentrations of Cl^- or NO_3^-
Sample opacity or color	Solvents: $CHCl_3$, methyl ethyl ketone, CCl_4, etc.
Precipitation	Peroxide
Fingerprints on vial	Incorrect fluor
Phase separation	Expired fluor
Light leaks into instrument	Contaminated fluor
Inadequate dark adaptation	
Temperature changes	
Different vial composition	

MEASUREMENT OF ^{55}FE IN RADIOACTIVE WASTE SOLUTIONS. The separation techniques for iron generally use nitric and hydrochloric acids. Both of these acids are eliminated prior to the preparation of the cocktail by boiling down the solution with phosphoric acid. Nitric acid can decompose in room light giving rise to the gas N_2O_4, which can impart a brown color to the solution. High concentrations of chloride can act as electron scavengers in the solution. Both these conditions yield quench. Removing them with phosphoric acid maintains the solution acidity (so the iron does not precipitate) and does not act as a quench agent.

SAMPLES IN CONCENTRATED NITRIC ACID. If samples must be made with high concentrations of nitric acid, they should be measured shortly after preparation, to avoid fluor decomposition. The samples need to have their quench compared to standard samples of the same acid composition and short time following preparation.

TRITIUM IN RAINWATER. Some methods of collecting rainwater involve funneling from a large surface area (like a roof) into a collection bottle through a spout. Rainwater itself contains many contaminants, such as carbon dioxide, sulfur dioxide, and polycyclic aromatic hydrocarbons (PAHs from fossil fuel combustion), which can act as significant quench agents. Furthermore, the surface through which the water is collected may contain accumulated particulate matter that also can affect the quench. Distilling the sample would minimize the effect of their quench. Without this, the quench would be increased and the "apparent" value would have a significant uncertainty associated with it.

18.5.6 Summary Guidance on Instrument Calibration, Background, and Quality Control

Radiation detectors and nuclear instrumentation, such as spectrometry systems, should be

calibrated and maintained according to protocols and procedures documented in the laboratory's standard operating procedures and quality manual. The important calibration parameters, the performance criteria used to monitor these calibration parameters, and the frequency of re-calibrations should be addressed in these documents. Another important parameter that should be addressed is the detector background. Detector background measurements should be taken at an appropriate frequency for the purposes of determining the net count rate of a test source and for controlling contamination.

The following subsections discuss the important calibration and monitoring parameters associated with nuclear instrumentation in common use at radioanalytical laboratories. At the end of each subsection, a table provides some examples of performance criteria for the measurement parameters and the frequency of monitoring of these parameters. The information in these subsections conforms to ASTM E181, ANSI N42.12, and NELAC (2002) and uses the input of the ASTM D19.04 Subcommittee on Methods of Radiochemical Analyses for Radioactivity in Water. A few important concepts should be considered when reviewing the following sections and summary Tables 18.5 through 18.8:

- NIST-traceable radionuclide sources (or traceable to a national standards body) are to be used for all calibrations when possible (see Chapter 15, *Quantification of Radionuclides*). Sources used for QC checks do not have to be NIST-traceable.

- The frequency of performing QC detector-response measurements, or evaluating a detector background, is related to the risk (probability) that a laboratory will accept for not detecting an instrument problem or a change in background, given a certain number of samples analyzed. The acceptable risk for not detecting a problem may vary from one laboratory to another. If an instrument QC response check is performed once every 10 samples (test sources), then there is a possibility that nine samples may be counted on an instrument not meeting quality specifications before a problem is detected. Therefore, it is more appropriate to establish the frequency of instrument QC based on the number of samples processed rather than on time schedules. The examples of instrument QC frequencies presented in the following sections are considered practical for most laboratories.

- Loss of control results from a calibration performance criterion not being met, any repair or maintenance that could affect a calibration parameter, and any event (such as sudden loss of power) that could affect calibration.

- Even without loss of control, a counting or spectrometry system should be re-calibrated for test-source radionuclides, matrices, and counting geometries at a frequency consistent with specifications delineated in the laboratory's quality manual.
- For an accurate measurement of a detector's counting efficiency and resolution, as well as for a detector's QC response checks, the relative counting uncertainty (1σ) of the measurement (net count or net response) or in the individual peaks associated with spectrometry systems

should be 1 percent or less.

- Detector background measurements are used for the calculation of a net measurement response and for detector contamination control. A net measurement response is calculated using a long-duration detector background measurement in order to minimize the counting uncertainty of the measurement. Contamination control background measurements typically are taken more frequently and are of shorter duration than those for net measurement response applications. To determine possible gross contamination, the results from the contamination control background measurements should be evaluated statistically and compared to the long-duration background results.

18.5.6.1 Gas Proportional Counting Systems

CALIBRATIONS

Three parameters should be considered when calibrating a gas proportional counting system:

- Operating voltage settings on the alpha and beta voltage plateaus,
- Detector counting efficiencies, and
- Crosstalk factors.

Initially upon instrument setup, the manufacturer's specifications for these three parameters should be verified. It should be noted that the manufacturer's specifications may be based upon unique calibration sources and operating conditions that may not be similar to those used when analyzing test sources. For example, the manufacturer's detector efficiency and crosstalk factors may be based on electroplated alpha and beta sources. For most laboratories, the typical test source for GP counting is not an electroplated source, so the reference alpha and beta radionuclides for calibration are not the same as the radionuclides used by the manufacturer in developing the specifications. However, the detector's alpha and beta voltage plateau settings typically are not changed after instrument setup. The alpha and beta voltage plateau settings are selected from plots of the applied detector voltage versus the observed count rate for pure alpha and beta sources (see Chapter 15, *Quantification of Radionuclides*).

The next parameters to evaluate are the detector's alpha and beta counting efficiencies for various source geometries. Initially, the manufacturer's detector efficiency for both alpha and beta counting modes should be verified using electroplated sources. (Typical electroplated calibration sources include ^{99}Tc and ^{90}Sr for beta sources and ^{230}Th or ^{241}Am for alpha sources.) A detector's counting efficiency should be determined for each radionuclide and method used to analyze test sources. The detector efficiency should be determined for new or changed method protocols and loss of instrument control. For test sources having mass loading, an efficiency curve or mathematical function that describes the detector efficiency versus mass loading, consistent with the expected test source mass range, should be developed. For any mass in the

expected calibration range, the 95-percent confidence limits for the detection efficiency should be within 10 percent of the fitted value for alpha sources and within 5 percent of the fitted value for beta sources.

The crosstalk factors for the alpha counts into the beta channel (alpha crosstalk) and for the beta counts in the alpha channel (beta crosstalk) should be determined when applicable. The manufacturer's specifications for the crosstalk factors using electroplated sources should be verified prior to test source processing. Typical manufacturer specifications for electroplated sources are less than 1 percent alpha counts in the beta channel for ^{210}Po and less than 0.1 percent beta counts in the alpha channel for ^{90}Sr/Y. The alpha crosstalk factor will vary according to the crosstalk parameter setup, decay scheme of the alpha emitting radionuclide, and the mass (weight) of the source. Verify the manufacturer's alpha crosstalk factor using the radionuclide and crosstalk parameters setting specified by the manufacturer. The alpha crosstalk factor for other radionuclides and source masses should be determined for each method, preferably at the same time as determining the detector counting efficiency factors or efficiency versus source mass function. The crosstalk factors may be method specific and should be determined during initial calibration and after re-calibrations.

BACKGROUND

A detector's background should be determined immediately after calibration and at the instrument settings established for each method. An accurate estimate of a detector's background is needed to determine the net count rate of a source. For this application, a very long background, with respect to the nominal counting time for the test sources, typically is needed depending on the required detection limit. One approach for making long-duration background measurements is to count a clean test-source mount long enough to achieve a relative counting uncertainty (1σ) of less than 10 percent for alpha measurements and less than 3 percent for beta measurements. Alternatively, the counting time for a long-duration background measurement should be between one and four times the nominal counting duration of test sources for a given matrix and application. A long-duration background measurement should be conducted on a monthly basis. A statistical test should be used to determine if the detector's background has changed from the initial background determination.

When required, a detector may be evaluated frequently for gross contamination using a short-duration counting interval. When the counting duration of test sources is short (less than one hour), a short-duration background measurement should be conducted prior to processing test sources. When the test-source counting time is longer, the background time interval should be the same as the test sources, and the background should be determined before and after a sample (test source) batch.

CALIBRATION QC CHECKS

Once a GP counting system has been calibrated, the detector's response should be monitored frequently to determine if a significant change has occurred. Typically, a tolerance limit or control chart (Section 18.3, "Evaluation of Performance Indicators") is established to monitor the detector's response and to flag responses that exceed pre-established control limits. A tolerance limit or control chart should be established immediately after the initial counting efficiency calibration, and after instrument loss of control. A tolerance limit or control chart should be set at ± 3% or 3σ. Once a chart has been established, an instrument or detector response check should be performed after a counting-gas change and daily for short test-source counting intervals. For longer test-source counting times, a detector response check for a multi-sample shelf unit should be conducted prior to test source counting, while a detector response check for a sequential sample counter should be performed before and after the sample batch.

TABLE 18.5 — Example gas proportional instrument calibration, background frequency, and performance criteria

Calibration Need	Measurement Parameters	Performance Frequency	Performance Criteria
Calibration	Alpha and beta plateaus and operating voltages	Prior to initial use and after loss of control.	Verify manufacturer's specifications. Plot voltage vs. count rate to determine proper operating voltages.
	Alpha and beta crosstalk factors	Prior to initial use, after loss of control, and upon incorporation of new or changed instrument settings.	Verify manufacturer's specifications. Determine crosstalk factors for each nuclide, matrix and method. For mass-loaded test sources, determine crosstalk factors for the nuclide as a function of test source mass
	Detector counting efficiency	Prior to initial use, after loss of control, and upon incorporation of new or changed instrument settings.	Verify manufacturer's specifications. A 1σ counting uncertainty of ≤1% should be achieved for all detector efficiency determinations.
	a) Weightless sources	Prior to initial use, after loss of control, and upon incorporation of new or changed instrument settings. Recalibrate per quality manual.	Zero-mass sources using the same radio-nuclide of interest.
	b) Mass-loaded sources	Prior to initial use, after loss of control, and upon incorporation of new or changed instrument settings. Recalibrate per quality manual.	For radionuclide of interest, establish mathematical function (curve) of detector efficiency vs. source mass loading. 95% confidence limit of the fitted function (curve) over the calibration range to ≤10% and ≤5% uncertainty for alpha and beta, respectively.
Detector Background		Determine alpha and beta background initially and after efficiency calibration.	Verify manufacturer's specifications.
a) Short count for gross contamina-tion control	Detector background using a contamination-free source mount	Daily for short test-source counting intervals. For longer test-source counts, use the same interval as the test sources before and after a sample batch.	Use a statistical test to determine if the new background count rate is different from the initial (at time of calibration) long background count rate.

Calibration Need	Measurement Parameters	Performance Frequency	Performance Criteria
b) Long count for background subtraction of test sources and blanks	Detector background using a contamination-free source mount	Monthly when system is in use.	Establish a background count rate value based on measurement uncertainty or count a long background for a time interval that is 1 to 4 times the typical test-source counting time. Use statistical testing to determine a change in the long background count rate value.
Calibration QC check – detector response check	Count rate using a radionuclide source of appropriate emission and energy	Develop detector response control chart immediately after calibration and loss of control. Perform detector response check daily, prior-to-use, or bracketing a sample batch depending on test source counting time.	Count QC source to reach net 1σ counting uncertainty of ≤1%. For all detector response checks, compare performance to control chart or tolerance limits: ±3σ or ±3%.

18.5.6.2 Gamma-Ray Detectors and Spectrometry Systems

CALIBRATIONS

Three parameters should be considered when calibrating a gamma-ray (photon) detector or spectrometry system. These include the energy (gain and base) calibration, energy resolution, and the detector efficiency calibration for a particular geometry and matrix combination. Initially upon instrument setup, the manufacturer's specifications for the latter two parameters should be verified for a detector. It should be noted that verification of the manufacturer's specifications may require different instrument settings, sources, and geometries compared to those used during normal test-source analyses.

The energy calibration covers the photon energy range of the desired radionuclides expected in test sources. This calibration involves adjusting the gain of the system amplifier so that a specific slope calibration can be achieved (e.g., 0.5 keV/channel). At least two widely spaced photon peaks are needed to determine the energy calibration (Section 17.3.1, "Gamma Spectrometry"). It should be noted that verification of the manufacturer's specification for detector resolution may require a difference in energy calibration (e.g., 0.10 or 0.25 keV per channel) compared to the energy calibration settings used for typical test sources. For most modern spectrometry systems, the instrument energy parameters are very stable. The energy calibration parameter should be monitored as appropriate to support data-reduction algorithm requirements for energy fit and resolution. Typically, the determination of the energy calibration parameter can be made from the data acquired from the daily detector response QC measurement. A tolerance limit on the maximum energy calibration deviation, rather than a QC chart, can be used as an alternate to verifying amplifier output voltages. A pass-fail criterion for peak position also should be established. For example, the channel number that the ^{137}Cs 661.6 keV peak can change should be less than two channels. Some software applications adjust the energy of the gamma-ray spectrum using the daily energy calibration data. Such applications do not require changes in the settings of the

system's electronics.

The manufacturer's detector resolution, expressed as the FWHM in keV at specific photon energies, should be verified prior to use. Manufacturers of detector systems routinely establish an energy calibration of 0.25 or 0.10 keV/channel by adjusting the gain of the detection system amplifier. The FWHM and the peak-to-Compton ratio are both measured at a specified distance from the detector. Analytical laboratories frequently calibrate energies at approximately 0.50 keV/channel. Thus, prior to initial calibration or when re-calibration is necessary, the analytical laboratory should duplicate the manufacturers conditions for FWHM and peak-to-Compton ratio at the manufacturers stated initial conditions for the detector. It should be noted that the detector resolution varies with energy (Chapter 15) and can be affected by such factors as temperature, humidity, vibration, poor connectors, or poor line-voltage conditioning. The QC check sources used for the detector response check typically are used for resolution measurements during test-sources analyses. For a combined detector response and resolution check, the radionuclides selected for the QC source have photon energies that normally cover the low, middle, and high energies of the desired range (e.g., ^{241}Am, ^{137}Cs, and ^{60}Co). The photon energies selected for the resolution check should be sufficiently separated to avoid other interfering peaks. If the energy calibration settings for routine test source analyses is 0.5 keV per channel or greater, a resolution check may only indicate gross or substantial changes in a detector's resolution (e.g., greater than 10 to 20 percent). Photopeaks with greater than 10,000 counts are needed for routine resolution checks. Once the routine (operational) resolution value has been determined, limiting the maximum resolution deviation with an acceptable tolerance limit may be more suitable than using a QC chart. QC verification of resolution should be performed on a pass-fail basis. Since the FWHM varies as a function of energy, each peak should have its own acceptance criterion.

The peak-to-Compton ratio is an important characteristic of the detector that needs to be compared with the manufacturers specification upon initial detector calibration. This ensures that the maximum sensitivity for full energy peak (FEP) analysis is achieved, and the correct semiconductor crystal has been installed in the detector housing. See Section 15.6.2.1, "Detector Requirements and Characteristics," for the definition and technical basis for the peak-to-Compton ratio determination. This parameter needs to be checked during initial detector setup or prior to detector recalibration.

The next parameter that should be evaluated is the detector's efficiency response as a function of energy and matrix. The manufacturer's specification for detector efficiency is relative the efficiency of a 76 × 76 mm NaI detector responding to to ^{57}Co, ^{137}Cs, and ^{60}Co point sources at a distance of 25 cm from the detector. The standard NaI efficiency for this detector size and a ^{60}Co point source is 0.1 percent. (Gilmore and Hemingway, 1995). For each geometry/matrix combination used for test-source analyses, a gamma-ray efficiency versus energy response function (curve) must be determined. It is important that the same geometry and matrix be used for the calibration and test sources. This includes the container for these sources, as well as their physical placement relative to the detector. The efficiency check should span the energy range of

radionuclides of interest. For commercially available mixed radionuclide calibration sources, 10 data points per calibration curve is typical, covering the range of 59 keV (^{241}Am) to 1,836 (^{88}Y) keV. The 95 percent confidence limit of the fitted curve should be under 8 percent over the calibration energy region. A detector response QC chart should be established immediately after the first calibration for the detector.

DETECTOR BACKGROUND

A detector's background should be determined immediately after calibration with or without a counting container, depending on the inherent radionuclide activity levels in the counting container. An accurate estimate of a detector's background in a radionuclide photopeak is needed when determining the net photopeak count rate of a source. For this application, a very long background with respect to the nominal counting time for the test sources typically is needed, depending on the required detection limit. One approach for making long-duration background measurements is to count a clean test source mount to achieve a relative counting uncertainty (1σ) for major photopeaks that is ≤ 10 percent. Alternatively, the counting interval for the long count should be between one and four times the nominal counting interval of the test sources. A long detector background measurement should be conducted on a monthly or quarterly basis. A statistical test should be used to determine if the detector background in a photopeak has changed significantly from the initial background determination. Acceptable integrated background values will be defined by the measurement limits desired by the analytical method. The statistical criterion that constitutes a significant change should be stated in the laboratory's quality manual.

When required, the detector's background may be evaluated for gross contamination on a frequent basis using a short counting interval. Once the long background count rate has been determined, a shorter background count can be made and the results compared statistically to the long background count rate to determine possible detector contamination. For the short background, the energy region between about 50 and 2,000 keV is integrated. The counting time for the short background count should be set so that the relative counting uncertainty (1σ) of the integrated counts is ≤ 3 percent. A limit in the deviation of the integrated background value may be set using a tolerance limit or control chart. It should be verified that no extraneous peaks are identified, indicating lower-level contamination (i.e., no new peaks in the short background spectrum compared to previous spectra)

CALIBRATION QC CHECKS

After the initial detector calibration, a control chart or tolerance limit should be established (Section 18.3, "Evaluation of Performance Indicators"). Such a chart may be generated using a noncalibrated, but reproducible geometry. This source does not necessarily need to be a primary-grade calibration source, but a sealed source that is well characterized and stable. The purpose of this QC source is to validate that the detector performance is reproducible on a day-to-day basis for the detector efficiency, energy response, and resolution. These characteristics can be used on

a relative basis for the QC source as long as it is stable and sealed, so that its only change will be as the result of radioactive decay (which can be accounted for mathematically). It must cover a reasonable energy range (low, middle, and high energies), and the generated QC data should have a relative 1σ uncertainty of under 1 percent. The detector-efficiency QC response check should have a tolerance limit or control chart set at ± 3 percent or 3σ. Monitoring of gamma-ray energy resolution (as measured by the FWHM) typically is a tolerance-limit measurement. Thus, an upper bound for this value at specified energies in the calibrated range will serve as the indicator of this parameter. For example, if the acceptable limit for FWHM at the 1,332 energy peak of ^{60}Co is 2.2 keV, any value greater than 2.2 keV at this energy would cause the system to be out of tolerance. A similar situation exists for the energy QC. An upper and lower limit, based on temperature drift of the electronics and detector system, should be used as a tolerance limit. Thus, the example of the ^{60}Co peak the band of acceptable energies that the instrument measures could be from 1,331.5 to 1,333.4 keV. The small changes in parameters such as these do not significantly affect the measurement. The idea of the tolerance limit here puts a bound where an effect can indicate performance issues. It is important to note that some gamma-ray spectrometry software systems use information obtained from the daily energy QC measurement to adjust for the energy response difference when analyzing a spectrum. Any changes to the configuration, integrity or geometry of the QC standard due to age warrants an investigation of its validity.

TABLE 18.6 — Example gamma spectrometry instrument calibration, background frequency, and performance criteria

Calibration Need	Measurement Parameters	Performance Frequency	Performance Criteria
Calibration	Detector energy calibration and high resolution peak to Compton measurements	Prior to initial use and after loss of control	Peak resolution; peak-to-Compton ratio (actual vs. manufacturer); equations for energy calibration; and shift in energy vs. channel number.
	Counting efficiency: matrix- and geometry-specific	Prior to initial use, after loss of control, and as required by quality manual.	Efficiency vs. energy for each geometry/ matrix. 95% confidence limit of the fitted function: ≤8% over energy range.
Background – Short count for controlling gross contamination	Integrate spectrum from ~50–2,000 keV	Daily or prior to use.	No extraneous peaks; tolerance limit or control chart: ± 3% or 3σ .
Background – Long count for subtracting background from blanks or test sources	Establish background peak/ region-of-interest (ROI) count rate and uncertainty for inherent radionuclides in detector, shield, and the counting geometry vessel.	Monthly or quarterly	Statistical test of successive counts and count rates for ROI show no significant difference.
Calibration QC check – Detector response	Energy, efficiency, and resolution	Daily or prior to use	Verify peak shift within tolerance limit; verify efficiency within control parameters; verify resolution in tolerance limit.

18.5.6.3 Alpha Detector and Spectrometry Systems

CALIBRATIONS

Three parameters should be considered when calibrating an alpha detector or spectrometry system. These include the energy (gain and base) calibration, energy resolution, and the detector efficiency for a particular combination of geometry and matrix. Additionally, a detector's leakage current typically is monitored to detect detector problems and possible detector-chamber light leaks. The manufacturer's specifications for detector resolution and efficiency should be verified initially upon instrument setup. Verifying the manufacturer's specifications may require different instrument settings and sources compared to those used during normal test-source analyses. The instrument setup and source geometry details normally are included in the manufacturer's documentation for a semiconductor alpha detector. The manufacturer's detector resolution (FWHM) in MeV is measured using an electroplated ^{241}Am point source in a near vacuum.

The energy calibration should be applicable to the alpha energies of the radionuclides expected in the test sources. This calibration involves adjusting the gain of the system amplifier so that a specific energy slope calibration can be achieved to cover a desired energy range. A typical energy range is between 3 and 8 MeV for long-lived radionuclides and between 3 and 10 MeV for short-lived radionuclides. At least two widely spaced alpha peaks are needed to determine the energy calibration. An energy calibration should be a linear response. However, the acceptable deviation in the energy gain (MeV per channel) depends on the total number of channels and the range of the energy spectrum.

A detector's peak counting efficiency should be determined for each test-source geometry/matrix combination that will be used. Calibration source mounts should be equivalent to the test-source mount (electroplated or microprecipitate) and have the radionuclide of interest or a radionuclide with about the same alpha energy. Most radioanalytical methods using alpha spectrometry incorporate a radioisotope tracer (radiotracer) into the sample processing scheme as a means to determine the sample-specific, chemical-yield detector-efficiency factor. For these methods, a separate detector efficiency calibration is not needed. When radiotracers are not used to determine the chemical-yield-to-detector efficiency factor, a detector should be calibrated for each test-source mounting geometry according to the frequency specified in the laboratory's quality manual. For this calibration, the peak efficiency should be determined using the average of at least two alpha peaks. When measuring a detector's counting efficiency, the source should be counted sufficiently long so that the relative uncertainty (1σ) of the alpha peak(s) count is ≤ 3 to ≤ 1 percent.

DETECTOR BACKGROUND

A detector's background should be determined immediately after detector installation, instrument setup, detector calibration, or loss of control. The background counts in an alpha peak or a region of interest for the expected radionuclides should be integrated. A blank test source mount (filter

medium or blank electroplated mount) should be counted for a time interval between one and four times the typical test-source counting time. A detector background measurement should be conducted on a monthly basis, and the results tracked. When test sources contain certain radionuclides that may contaminate the detector (see Chapter 15), a background should be taken after counting the test source. A statistical test should be applied to determine if the detector background in a photopeak or region of interest has changed compared to the initial background determination. Acceptable integrated background values will be defined by the measurement limits desired by the analytical method.

CALIBRATION QC CHECKS

When no radiotracer is used in a method, a detector efficiency determination should be performed at least monthly. The detector efficiency parameter should be recorded and evaluated for changes using a tolerance limit or control chart. The detector efficiency QC response check should have a tolerance limit or control chart set at ± 3% or 3σ. In addition, when a radiotracer is not used, a spectral energy response should be performed weekly.

Frequent use of a calibration source may lead to progressive contamination that may become significant, as a result of atom recoil from the source (Chapter 15). An electronic pulser may be used to check the spectrometry system, but not all parameters will be evaluated.

TABLE 18.7 — Example alpha spectrometry instrument calibration, background frequency, and performance criteria

Calibration Need	Measurement Parameters	Performance Frequency	Performance Criteria
Calibration	Energy and FWHM peak resolution	Prior to initial use and after loss of control.	Verify manufacturer's specifications for alpha peak resolution and detector leakage current.
	Detector counting efficiency	Prior to initial use, after loss of control, and upon incorporation of new or changed instrument settings. Nonradiotracer applications – calibrate per quality manual For radiotracer applications, use radiotracer with every test source.	Verify manufacturer's specifications point-source efficiency. Nonradiotracer applications, calibrate each test source mounting geometry. For radiotracer and nonradiotracer applications, 1σ relative counting uncertainty ≤ 3% to ≤ 1%.
Detector Background	Detector background – ROIs or alpha peaks	Prior to initial use or after initial calibration and monthly.	Verify manufacturer's specifications. Count a blank test -source mount (filter medium or blank electrodeposited mount) for at least 1–4 times the typical test-source counting time and determine the ROI or alpha peak background levels for background subtraction and contamination control. Track background for each radionuclide's ROI or alpha peak. Use a statistical test to determine a change in the long background count rate value for a ROI or alpha peak.

Calibration Need	Measurement Parameters	Performance Frequency	Performance Criteria
Calibration QC check – detector response check	Determine peak location, resolution, and ROI/alpha peak efficiency (where counting efficiency is an analytical requirement) using at least two alpha peaks.	When radiotracers are used routinely, the radiotracer can estimate the peak location, gross peak resolution, and provide the detector efficiency–chemical-yield factor. When no radiotracer is used, a detector efficiency check should be performed at least monthly and an energy check weekly.	For nonradiotracer detector response checks, use a tolerance limit or control chart: ±3% or 3σ.

18.5.6.4 Liquid Scintillation Systems

CALIBRATIONS

Following the setup of a liquid scintillation (LS) counting system, the manufacturer's specifications for counting efficiency should be verified with the appropriate reference radionuclides sources, typically unquenched LS cocktails tagged with ^{3}H and/or ^{14}C. As part of the instrument setup, the energy regions of interest (ROIs) or energy windows for the beta spectra of the radionuclides should be established. A tolerance limit or QC chart can be prepared at this time using unquenched LS standards.

The LS counting system should be calibrated specifically for a radionuclide/method application. Verify that the recommended dark-adapt time for each cocktail used in the analyses is consistent with the recommendation of the instrument or cocktail manufacturer. For method calibrations, two different approaches are taken commonly to determine the detector efficiency. These include the development of an efficiency-response/quench curve and the standard addition approach. When establishing a quench curve, a minimum of five calibration sources of different quench factors should be used, and the individual calibration sources should be counted to give a ROI relative counting uncertainty (1σ) of less than 1 percent. A mathematical function and quench curve should be developed so that the 95 percent confidence limit of the function is less than 5 percent over the expected quench range of the sources. For the standard addition approach, where a spike of the radionuclide of interest is added to a duplicate test source (or the original test source after the first analysis), the activity of the spike should be at least four times the anticipated maximum radionuclide activity in a test source. Such standard addition measurements assure that an unknown quench agent or interferent is not having an appreciable affect on the test source quench. The spiked test sources should be counted so that the ROI relative counting uncertainty is less than 3 percent. The deviation in duplicate spiked test source measurements should be evaluated statistically using the methods in Chapter 7 (*Evaluating Methods and Laboratories*) for matrix-spiked duplicates. This ensures that sample homogeneity and sample handling practices are not appreciably affecting the sample analysis.

INSTRUMENT BACKGROUND AND METHOD BLANKS

For methods that have quenched test sources, a quenched method blank (or mean of several quenched blanks) should be used to determine the background count rate that is subtracted from the count rate of the quenched test sources in a batch. A method background is determined by counting a blank sample that has been taken through the analytical process for the radionuclide of interest and determining its quench. When prepared in this manner, the blank will have a quench value similar to that of the test sources in the batch having the approximately the same quench factor. The counting interval of the blank should be the same or longer than the counting interval of test sources in the batch. Multiple quenched blank measurements should be made to establish a mean quenched-background value and standard uncertainty of the mean (standard error of the mean). These parameters should be used to determine the net count rate (and combined standard uncertainty) of test sources within a batch of samples. The ROI count rate of the quenched blank test source (processed with each batch of test sources) should be recorded and monitored. A statistical test is recommended to determine a change in the quenched background from batch to batch.

For the standard addition approach to analyzing test sources, a blank sample should be processed with each batch of samples. The counting interval of the blank should be the same or longer than the counting interval of test sources in the batch. The efficiency corrected blank activity (or mean of several batches) should be subtracted from the activities of the test sources uncorrected for chemical yield.

Longer instrument backgrounds with unquenched blank test sources may be taken for instrument-contamination control and to detect light leakage or photomultiplier tube degradation. This background measurement, which is the integral of the total energy spectrum, should be taken after initial instrument setup and monthly thereafter. The counting interval should be sufficiently long to reach an integrated spectrum count that has a relative 1σ counting uncertainty of about 1 percent. The background data should be recorded and monitored. A statistical test to determine a change in the long integrated background count rate value is recommended.

CALIBRATION QC CHECKS

Once a liquid scintillation counting system has been calibrated, the detector's response should be monitored frequently to determine if a significant change has occurred. Typically, the unquenched reference radionuclides test sources (^{3}H and/or ^{14}C) provided by the manufacturer for instrument setup are used for the QC check sources. The detector's response, measured as the integrated counts in the energy ROIs for the beta spectra of the radionuclides, should be established. A tolerance limit or control chart (Section 18.3) is used to monitor the detector's response and to reveal changes in response that exceed pre-established control limits. A tolerance limit or control chart should be established immediately after the instrument setup and after instrument loss of control. Normally, a QC source is counted to reach a relative 1σ counting

uncertainty of under 1 percent in the ROI. The detector efficiency QC response check should have a tolerance limit or control chart set at ± 3 percent or 3σ. Once a tolerance limit or control chart has been established, an instrument/detector response check should be performed before each sample batch for short test-source counting intervals, and before and after a sample batch for longer counting intervals.

TABLE 18.8 — Example liquid scintillation counting systems calibration, background frequency, and performance criteria

Calibration Need	Measurement Parameters	Performance Frequency	Performance Criteria
Calibration	ROI calibration with unquenched reference standards (typically ^{3}H and ^{14}C)	Prior to initial use and after loss of control and recalibrate per quality manual.	Verify sealed standards activity. Energy distribution of unquenched standard matches manufacturer's.
Method calibration (determining quenching)	Quench curve (at least five points) for each radionuclide and LS cocktail matrix.	Prior to method application, matrix, and cocktail changes. Recalibrate per quality manual.	Count individual calibration source to achieve ROI (1σ) measurement uncertainty of ≤1%. 95% confidence limit of the fitted function <5%
	Internal standard or standard addition – radionuclide of interest.	Add a spike to a duplicate processed sample or add a spike to a sample that has been counted and then recount.	Statistically evaluate replicate test-source analyses.
Background	Method background – quenched.	Each batch.	Use a statistical test to determine a change in the quenched background ROI count rate value.
	Long count background-unquenched blank.	Prior to initial use and monthly.	Monitoring of detector/ instrument contamination and electronic degradation based on integrated counts of entire spectrum.
Calibration QC Check – detector response check	ROI for unquenched reference standards (typically ^{3}H and/or ^{14}C)	Prior to use for short counting intervals. Before and after a test source batch for longer counting intervals.	Control chart or tolerance limit: ± 3σ or ± 3%.

18.5.7 Non-Nuclear Instrumentation

Radionuclides can also be measured using non-nuclear instrumentation such as mass spectrometry, fluorimetry, and phosphorimetry. These methods of analysis are discussed briefly in Chapter 15, *Quantification of Radionuclides*. Analysts can apply many of the laboratory QC techniques discussed in Sections 18.3, 18.4, and 18.6 because they are basic to any laboratory method. A quality program using statistically based control charts of the performance indicators will identify out-of-control situations, assist in improving laboratory performance, and aid in identifying the causes of trends and biases for any laboratory method. Analysts also need to

consider detection capabilities, radionuclide equilibrium, half-life, interferences, and blind samples when using non-nuclear instrumentation.

18.6 Related Concerns

18.6.1 Detection Capability

Issue: The *detection capability* of an analytical procedure is its ability to distinguish small amounts of analyte from zero (Chapter 20). The detection capability of a procedure can be estimated nominally and will depend on many factors.

Discussion: In radioanalysis, the most commonly used measure of detection capability is the minimum detectable concentration (Chapter 20). The MDC is defined as the smallest concentration of an analyte that has a specified probability of detection. The MDC is usually estimated as a nominal scoping performance measure of an analytical procedure, but a sample-specific version is reported routinely by many laboratories.

Detection capability is affected by many factors, including counting times, instrument background levels, aliquant volume, yield, decay times, and interferences. The nominal MDC is presumably based on conservative assumptions about these factors, but measurement conditions vary. The sample-specific MDC is calculated using the actual measured values of all these factors. A high MDC by itself does not indicate that a sample result is invalid or that it cannot be used for its intended purpose. However, if an analysis fails to detect the analyte of interest and the sample-specific MDC is greater than a detection limit required by contract or other agreement, it may be necessary to reanalyze the sample in a way that reduces the MDC. Such decisions should be made case-by-case, since it is not always cost-effective or even possible to reanalyze a sample, or it may not be feasible to achieve the desired MDC.

Excursions: A high sample-specific MDC can be caused by many factors, including:

- Small sample aliquant;
- Low chemical/tracer yield;
- Short counting times;
- Long decay/short ingrowth time;
- High background or blank value; and
- Low counting efficiency or sample self-attenuation.

18.6.2 Radioactive Equilibrium

Issue: It is sometimes necessary to ensure that target radionuclides are in radioactive equilibrium with their progeny, or to establish and correct for disequilibrium conditions. This is particularly

applicable for protocols that involve the chemical separation of long-lived radionuclides from their progeny. This is also applicable for nondestructive assays like gamma spectrometry where photon emission from progeny is used to determine the concentration of the non-gamma ray emitting parent (see Attachment 14A following Chapter 14 for a more thorough discussion on radioactive equilibrium).

Discussion: Some radionuclides that have long physical half-lives decay to species whose half-lives are shorter by several orders of magnitude. Following chemical separation of the parent, the progeny can "grow in" within a time frame relevant to analysis and provide measurable radioactive emissions that should be considered in the analytical method. The condition where the parent and progeny radionuclide are equal in activity is called "secular equilibrium." An example is ^{226}R, a common, naturally occurring radionuclide in the uranium series with a half-life of about 1,600 years. ^{226}Ra is found in water and soil, typically in secular equilibrium with a series of shorter-lived radionuclides that begins with the 3.8-day-half-life ^{222}Rn and ends with stable lead. As soon as ^{226}Ra is chemically separated from its progeny in an analytical procedure via coprecipitation with barium sulfate, its progeny begin to reaccumulate. The progeny exhibit a variety of alpha, beta and gamma emissions, some of which will be detected when the precipitate is counted. The activity due to the ingrowth of radon progeny should be considered when evaluating the counting data (Kirby, 1954). If counting is performed soon after chemical separation, secular equilibrium will be substantially incomplete and a sample-specific correction factor should be calculated and applied. In some cases, it may be necessary to derive correction factors for radioactive ingrowth and decay during the time the sample is counting. These factors are radionuclide specific, and should be evaluated for each analytical method.

Secular equilibrium concerns also apply to non destructive assays, particularly for uranium and thorium series radionuclides. Important radionuclides in these series (e.g., ^{238}U and ^{232}Th) have photon emissions that are weak or otherwise difficult to measure, while their shorter-lived primary, secondary or tertiary progeny are easily measured. This allows for the parents to be quantified indirectly, i.e., their concentration is determined by measuring their progeny and accounting for the amount of parent-progeny equilibrium. The amount of parent-progeny secular equilibrium is fundamental to these analyses, and data should be scrutinized to insure that the amount is valid.

When several radionuclides from one decay chain are measured in a sample, observed activity ratios can be compared to those predicted by decay and ingrowth calculations, the history of the sample and other information. For example, undisturbed soil typically contains natural uranium with approximately equal activities of ^{238}U and ^{234}U, while water samples often have very different ^{238}U/^{234}U ratio. Data from ores or materials involved in processing that could disrupt naturally occurring relationships require close attention in this regard.

All numerical protocols (electronic and manual) should be evaluated to determine if there is bias

with respect to correction factors related to equilibrium concerns. This includes a check of all constants and units used to derive such correction factors, as well as the use of input data that unambiguously state the time of all pertinent events (chemical separation and sample counting). The analyst should ensure that samples requiring progeny ingrowth are held for sufficient time before counting to establish secular equilibrium. Limits for minimum ingrowth and maximum decay times should be established for all analytical methods where they are pertinent. For ingrowth, the limits should reflect the minimum time required to ensure that the radionuclide(s) of interest has accumulated sufficiently to not adversely affect the detection limit or uncertainty. Conversely, the time for radioactive decay of the radionuclides of interest should be limited such that the decay factor does not elevate the MDC or adversely affect the measurement uncertainty. These will vary depending on the radionuclide(s) and analytical method.

Excursions: Samples where equilibrium is incorrectly assumed or calculated will produce data that do not represent the true sample concentrations. It is difficult to detect errors in equilibrium assumptions or calculations. Frequently, it takes anomalous or unanticipated results to identify these errors. In these cases, analysts need to know the sample history or characteristics before equilibrium errors can be identified and corrected. Some samples may not be amenable to nondestructive assays because their equilibrium status cannot be determined; in such cases, other analytical methods are indicated.

Examples:

Isotopic Distribution – Natural, Enriched and Depleted Uranium: Isotopic distribution is particularly important with respect to uranium, an element that is ubiquitous in nature in soils and also a contaminant in many site cleanups. The three predominant uranium isotopes of interest are ^{238}U, ^{234}U, and ^{235}U, which constitute 99.2745, 0.0055, and 0.72 atom percent, respectively, of "natural" uranium,[3] i.e., uranium as found in nature (Parrington et al., 1996). However, human activities related to uranium typically involve changing the ratio of natural uranium by separating the more readily fissionable ^{235}U from natural uranium to produce material "enriched" in ^{235}U, for use in fuel cycle and nuclear weapons related activities.[4] Typical ^{235}U enrichments range from 2 percent for commercial reactor fuels to greater than 90 percent ^{235}U for weapons. The enrichment process also produces material that is "depleted" in ^{235}U, i.e., the uranium from which the ^{235}U was taken. While the ^{235}U concentrations of depleted uranium are reduced relative to natural ores, they still can be measured by several assay techniques. This gives rise to uranium with three distinct distributions of ^{238}U, ^{235}U, and ^{234}U, referred to as "natural," "enriched," and "depleted" uranium. Because ^{238}U, ^{235}U, and

[3] The "natural abundance" of ^{235}U of 0.72 atom percent is a commonly accepted average. Actual values from specific ore samples vary.

[4] Enriched and depleted refer primarily to ^{235}U.

^{234}U are alpha emitters with considerably different physical half-lives and specific activities, a measurement of a sample's total uranium alpha activity cannot be used to quantify the sample's isotopic composition or uranium mass without knowing if the uranium is natural or has been enriched or depleted in ^{235}U. However, if this information is known, measurement and distribution of the sample's uranium alpha activity can be used to infer values for a sample's uranium mass and for the activities of the isotopes ^{238}U, ^{235}U, and ^{234}U. This ratio can be determined directly or empirically using mass or alpha spectrometry, techniques which are time and cost intensive, but which provide the material's definitive isotopic distribution. It is often practical to perform mass or alpha spectrometry on representative samples from a site to establish the material's isotopic distribution, assuming all samples from a given area are comparable in this respect. Once established, this ratio can be applied to measurements of uranium alpha activity to derive activity concentrations for ^{238}U, ^{234}U, and ^{235}U data.

18.6.3 Half-Life

Issue: Radionuclides with short half-lives relative to the time frame of the analysis may decay significantly from the time of sample collection or chemical separation to counting. In some cases, this decay will cause the ingrowth of other short-lived radionuclides. In both instances, sample-specific factors should be applied to correct the sample's observed counting/disintegration rate. Also, determination of half-life could indicate sample purity. If radioactive impurities are not appropriately corrected, analytical errors will occur. Repetitive counting of the test source may confirm the radionuclide's half-life, and thus the radioactive purity of the test source.

Discussion: When assaying for short-lived radionuclides, data should be corrected for decay over the time period between sample collection and counting. For example, operating power reactors routinely assay environmental samples for ^{131}I, a fission product with about an eight-day half-life. Samples may be counted for several days up to two weeks, during which time their ^{131}I concentration is decreasing via radioactive decay. Using the eight-day half-life, the counting data should be decay-corrected to the ending time of collection in the field and corrected for decay before and during counting. If desired, environmental samples can be decay-corrected to a time other than sample collection.

Half-life considerations also apply to radionuclide ingrowth. Certain radionuclides are assayed by an initial chemical separation, which begins a time period over which their direct progeny are allowed to reach a near-secular equilibrium condition. This is followed by additional chemical separation, purification, and counting of the progeny. The degree of the progeny's ingrowth is calculated based on the radionuclides' half-lives and the elapsed time between the two chemical separations. Allowance should also be made for the progeny's decay from separation to counting and for decay that occurred while counting, if applicable. Two examples are the beta emitting radionuclides ^{228}Ra and ^{90}Sr: they are quantified by measuring the direct progeny of each, ^{228}Ac and ^{90}Y, respectively. For airborne concentrations of ^{222}Rn, sample collection and analytical

methods should incorporate concerns related to the short-lived progeny of other radon species, such as ^{220}Rn. Other half-life related considerations apply to alpha spectrometry when assaying samples for uranium and thorium chain radionuclides. Samples that have been allowed to sit for several weeks may accumulate short-lived radionuclides that have alpha emissions whose energies are in close proximity to target radionuclides. These can interfere with quantitative analyses of the target radionuclides. Chemical yield tracers used in alpha spectrometry, such as ^{234}Th and ^{232}U, can cause this effect due to their short-lived progeny and all chemical yield tracers should be scrutinized for this potential prior to their use in analytical methods. Radionuclide specific limits for minimum ingrowth and maximum decay times should be established for all analytical methods where they are pertinent. These should be based on limiting the adverse effect of such calculations on the detection limit and measurement uncertainty. All analytical methods involving computational corrections for radioactive decay of the target species should be evaluated relative to half-life and secular equilibrium related concerns. This evaluation should be incorporated in the routine data review process that is performed on all analytical results.

A good source for radionuclide half-lives and other nuclear data can be found at the Brookhaven National Laboratory's National Nuclear Data Center (www.nndc.bnl.gov/nndc/nudat/). Using this data source will ensure consistency within and among laboratories, and will provide analysts with the current values.

Excursions: Samples that are assayed by "non destructive" techniques like gamma spectrometry may provide indications of potential complications due to half-life related considerations. Because the assay provides information on photon emitting radionuclides in the sample, the analyst can develop appropriate corrections for half-life related phenomena. However, non-spectrometric techniques like gas flow proportional counting are essentially gross counting procedures that record all events without any indication of their origin. Therefore, these data should be evaluated to ensure they are free from half-life related considerations (e.g., radionuclide purity).

Samples with short-lived radionuclide concentrations at or near environmental background will experience elevated detection limits and increased measurement uncertainty if there is excessive elapsed time between sample collection and counting. Because of the magnitude of the additional correction (decay) factor for these samples, they usually have a larger measurement uncertainty compared to longer-lived radionuclides, given equal measurement and sample conditions and parameters.

18.6.4 Interferences

Issue: Chemical or radionuclide interferences can produce erroneous results or increased measurement uncertainty.

Discussion: Analytical samples, particularly environmental samples, are often chemically complex. This complexity may include chemical constituents that interfere with an analytical method to the point that they require modification of the method. Examples of modifications include limiting the size of the sample aliquant, quantifying interfering compounds through other analyses (radiometric and non-radiometric) and changing time periods to allow adequate ingrowth of target radionuclides or decay of interferences.

A common example is groundwater or well water that contains high concentrations of salts or dissolved solids, so that screening for gross alpha activity produces erratic or anomalous results. For such samples, it may be necessary to limit the aliquant volume with the resulting increase in detection limit and measurement uncertainty. There is a salt concentration at which this procedure cannot overcome the interferences and should not be used.

Samples that contain natural concentrations of stable or radioactive compounds that are added during an analytical procedure (e.g., carrier or tracer) may also cause interference problems. Because barium is used as a carrier, water samples that contain a high concentration of barium may provide inaccurate carrier yields when screened for alpha-emitting radium isotopes. Quantifying the sample's barium content prospectively via a non-radiometric technique (e.g., atomic absorption) would be required to correct for this interference. With respect to radioactive compounds, two examples are provided. The first involves the radiochemical procedure for determining ^{228}Ra in drinking water that separates radium via coprecipitation with barium sulfate. The precipitate is allowed to come to equilibrium with its direct progeny ^{228}Ac, which is separated via co-precipitation with yttrium oxalate, purified, mounted and counted. The yttrium precipitate also carries ^{90}Y, the direct progeny of ^{90}Sr, a fission product often found in environmental samples as a result of atmospheric weapons testing and nuclear fuel cycle activities. The results of samples assayed for ^{228}Ra that contain measurable amounts of ^{90}Sr require corrections because of the differences in half-lives (^{228}Ac with a 6-hour half-life versus ^{90}Y with a half-life of about 64 hours) or other parameters. The second example involves alpha spectrometry procedures that use tracers to determine chemical yield. For example, ^{234}Th is used as a chemical yield tracer for isotopic thorium analyses. The approach assumes that the sample's inherent concentration of the tracer radionuclide is insignificant such that it will not interfere with the tracer's ability to accurately represent the sample's chemical yield. Samples that contain measurable amounts of these radionuclides may produce excessive interference and may not be amenable to this procedure.

Alpha spectra should be checked for radionuclide interferences (e.g., a ^{232}Th peak in uranium spectra). If the ^{232}Th peak is present due to incomplete chemical separation, ^{230}Th may represent interference in the ^{234}U determination. Data should be corrected or the samples reanalyzed with better target-radionuclide purification.

Each analytical method should be evaluated with respect to interferences during the method-

validation stage. Such evaluations can be based on available information and, if properly documented, can serve as the basis for developing the range of applicability, which becomes an integral part of the protocol. Evaluating performance indicators aids in the identification of samples that have interferences. All performance criteria would be protocol specific, and have clearly established acceptance ranges that incorporate the potential interferences discussed above.

Excursions: Interfering elements can affect measurement results in several ways. For example, large amounts of non-analyte elements may overload ion exchange resins, affecting the resin's ability to collect all of the analyte. In addition, spiking elements, already in the sample prior to preparation, may cause matrix spike results to exceed acceptance limits.

Carrier/tracer yields exhibiting gradual changes that appear to be correlated with a batch or group of samples from the same sampling location may indicate potentially interfering conditions. A significant decrease in the carrier/tracer yield may indicate that the analytical method is not functioning as planned. Yields that are significantly low or in excess of 100 percent may be caused by competing reactions within the sample matrix, or by the presence of an inherent carrier or tracer within the sample.

For screening analyses, e.g., gross alpha or beta, large changes in counting efficiencies or erratic counting data can reflect the presence of salts. Samples of this type are hygroscopic and continue to gain weight following preparation as they absorb moisture from the air. These changes could be detected by reweighing the planchets directly prior to counting. These samples can be converted to oxides by carefully holding them over the open flame of a laboratory burner; however, this will cause losses of volatile radionuclides, such as ^{210}Po and ^{137}Cs, which have alpha and beta emissions, respectively. An alternative approach is to thoroughly dry each planchet, record the weight and count it immediately, followed by a post-counting weighing to ensure that the weight did not change significantly over the measurement period. This approach may not be practical for all laboratories.

18.6.5 Negative Results

Issue: When an instrument background measurement is subtracted from a measurement of a low-activity sample, it is possible to obtain a net activity value less than zero.

Discussion: Many factors influence the evaluation of negative results. The simplest case occurs when the background measurement is unbiased and both the gross counts and background counts are high enough that the distribution of the net count rate is approximately normal. In this case, normal statistics can be used to determine whether a negative result indicates a problem. For example, if a sample contains zero activity, there is a very small probability of obtaining a net count rate more than two-and-a-half or three standard deviations below zero (i.e., negative value). Since the combined standard uncertainty is an estimate of the standard deviation, a result

that is less than zero by more than three times its combined standard uncertainty should be investigated. In fact, if a blank sample is analyzed using an unbiased measurement process, negative results can be expected about 50 percent of the time. As long as the magnitudes of negative values are comparable to the estimated measurement uncertainties and there is no discernible negative bias in a set of measurements, negative results should be accepted as legitimate data and their uncertainty should be assessed. On the other hand, if a sample activity value is far below zero, there may be a reason to investigate the result. A large percentage of negative results may also indicate a problem, even if all of the results are near zero. When instrument backgrounds are extremely low, statistics based on a normal distribution may not be appropriate (Chapter 19).

A preponderance of results that are negative, even if they are close to zero, indicates either a systematic error or correlations between the results. If the results are measured independently, a pattern of negative results indicates a bias, which requires investigation.

Excursions: Negative results occur routinely when samples with low levels of activity are analyzed, but a result should seldom be more than a few standard deviations below zero. Possible causes for extremely negative results or for an excessive number of negative values include:

- Instrument failure (low sample counts or high blank counts);
- Positive bias in the background or reagent blank measurement;
- Overestimation of interferences;
- Wrong or inappropriate background data;
- Data transcription error; or
- Calculation error.

18.6.6 Blind Samples

Issue: The performance of the analytical method should be assessed independently on a regular basis. This assessment is achieved through the use of blind samples that provide an objective means of evaluating the laboratory's performance when analyzing specific analytes and matrices. Blind samples can be internal or external, and either single or double. External blind performance-testing (PT) samples (also called performance-evaluation, or PE, samples) are used for QA purposes and also can provide information that is useful to laboratory QC.

Discussion: A blind sample is a sample whose concentration is not known to the analyst, and whose purpose is to assess analytical performance. Regardless of their nature, blind samples are effective only when their contents are unknown to the analysts. The preparation of all blind and other performance assessment samples is usually designated as a QA function. The QA staff functions independently from personnel responsible for sample processing and analysis. Blind samples consist of a matrix routinely processed by the laboratory that contains a known amount

of one or more analytes (radionuclides). A blind sample also may take the form of a replicate sample that is submitted for analysis such that its composition and origin are unknown to the analyst. These can be split samples (if run in the same batch) or spiked samples, and are prepared and submitted by an independent group either within the organization (internal), or from an independent organization (external). Performance on blind samples should be an integral part of the laboratory's quality system, which includes routine evaluation of their analytical results against specific performance criteria. For example, analysis of blind samples should be evaluated for relevant performance indicators. Data that fall outside an acceptance criterion may indicate loss of control in sample chemical processing, radiometric determination (counting) or other aspects of the analytical process. The ability to prepare blind samples depends fundamentally on the ability to obtain the appropriate combination of matrix with a radionuclide of a well-known concentration, ideally traceable to NIST or other appropriate certifying body. Also important are the expertise and experience of the preparer of the blind samples, proven and verified methodologies used for the blind samples, and detailed documentation. The use of blind samples assumes that their physical, chemical and radiological nature are similar to routine samples and compatible with the analytical methods employed at the laboratory.

When the analyst is aware that the sample is a blind sample but does not know the concentration, these samples are called single blinds. The analyst may know what analytes the blind sample contains, but not the analyte's concentration. Single blinds and other internal samples of this type are generally prepared by an organization's QA personnel that are independent of the samples' analyses. External single blind samples are available and can be obtained from several sources.

A double blind sample is a PT sample whose concentration and identity as a PT sample is known to the submitter but not to the analyst. The double blind sample should be treated as a routine sample by the analyst, so it is important that the double blind sample be identical in appearance to routine samples. A replicate routine sample would be considered a double blind PT sample. However, samples having sufficient measurable analyte are the most desirable as double blind samples for measuring precision. In general, a double blind is thought to be a more rigorous indication of the laboratory's performance, since analysts and other laboratory personnel may take special precautions when analyzing known PT samples, in anticipation of the greater scrutiny associated with such samples. This should not happen with double blind samples, since there should be no way to distinguish them from routine samples. However, true double blind samples are difficult to prepare.

INTERNAL BLIND SAMPLES. Internal blind samples are prepared by the laboratory's QA personnel. Internal blind samples assess several aspects of the analytical process. They allow the laboratory to demonstrate that it can successfully process routine samples for a specific analysis; in other words, they get a measured result within accepted limits. They provide an auditable, empirical record against specific quality performance criteria. They also demonstrate the efficacy of analytical methods and areas in need of adjustment. Double blind samples can pose logistical problems. It may be difficult to prepare internal double blind

samples and submit them to the laboratory for analysis successfully disguised as routine samples. Certain replicate routine samples are the exception. Evaluation criteria should be established to identify when conditions are out of acceptance limits.

EXTERNAL BLIND SAMPLES. External blind samples are those prepared by an organization outside that laboratory. This may be helpful with respect to ensuring that the analyte concentrations are truly unknown to the analyst; external blinds may offer a greater variety of matrices and analytes than can easily be produced within the laboratory and augment the laboratory's internal quality control program. Alternatively, if external blinds are not appropriate to the laboratory's programs, they will be of limited utility.

If statistical differences between observed and known values typically arise, these should be investigated thoroughly, as they indicate areas where important details of the analytical process may have been overlooked. Often a laboratory's observed values agree with the known value within acceptable tolerances, but are biased high or low. Careful documentation of the laboratory's performance in this regard can assist in characterizing the fluctuations of a measurement system or analytical method. Like other performance indicators, large or sudden changes in bias require scrutiny.

Blind samples should be an integral part of the laboratory's quality control program and they should be processed according to a predetermined schedule. Important sources of external blind samples include the NIST Radiochemistry Intercomparison Program (NRIP), National Voluntary Accreditation Program (NVLAP/EPA), Food and Drug Administration, DOE Lab Accreditation Program (DOELAP), Quality Assessment Program (DOE QAP), Multi-Analyte Performance Evaluation Program (DOE MAPEP), and several commercial vendors.

Excursions: The excursions typically encountered with analytical methods for specific parameters (carrier/tracer recovery, lack of precision, elevated backgrounds, etc.) apply to blind samples as well. Additionally, instances where the analysis of external blinds produces values that do not agree with the known values, may indicate that instrument calibrations or other correction factors require reevaluation. Problems revealed by the analysis of blind blank samples can indicate a problem (e.g., bias, blunder) within the laboratory, or conditions where the current protocol is inadequate. Excursions discovered while analyzing samples from external PT programs should be addressed.

18.6.7 Calibration of Apparatus Used for Mass and Volume Measurements

Issue: Fundamental to all quantitative analysis is the use of the proper masses and volumes. Analysts should perform careful gravimetric and volumetric measurements (especially in the preparation of calibration solutions, test sources, and reagents) in order to achieve the desired levels of precision and bias in each analytical method. Therefore, laboratory balances and

volumetric glassware and equipment should be calibrated and checked periodically to maintain the desired method performance levels. This section discusses the calibrations of laboratory balances and volumetric glassware and equipment. See Chapter 19, Attachment F, for further discussion on mass measurements.

Discussion: Laboratory balances should be periodically calibrated and checked. Most balances are typically calibrated and certified by the manufacturer once a year. These calibrations are performed to achieve the manufacturer's specified tolerances for each balance. A calibration certificate is supplied to the laboratory. In addition to this yearly calibration, daily calibration checks should be performed by the laboratory. Some laboratories check the balances once a day or at the time of each use. Any balance failing the daily calibration check should be taken out of service. Ordinarily, ASTM E617 Class 1 or 2 masses are used to perform the daily calibration check, depending on application. Over time, daily wear and tear on the masses can affect calibration, so it is a good idea to get them periodically re-certified or to purchase new masses.

Volumetric glassware and equipment, especially those used in the preparation of instrument calibration solutions and laboratory control samples, should be calibrated to the desired level of accuracy. Calibration can either be performed by the manufacturer of the equipment or by laboratory personnel. Calibration certificates for volumetric pipets and flasks are provided by the manufacturer at the time of purchase. Borosilicate and Pyrex® volumetric glassware will hold its calibration indefinitely provided that it is not exposed to hydrofluoric acid, hot phosphoric acid or strong alkalis, and that it is not heated above 150 °C when drying. Any glass volumetric pipet with a damaged tip should be discarded or re-calibrated. The manufacturer of volumetric automatic pipetting equipment calibrates the equipment and provides a certificate at the time of purchase. The re-calibration of automatic equipment should be performed annually and can be performed by the manufacturer, calibration specialty companies, or in-house laboratory personnel. Outside calibration services should provide a calibration certificate.

Laboratory personnel can calibrate and check volumetric apparatus using procedures like those specified in ASTM E542. Typically calibrations use volumes of water and are gravimetrically based. Volumes are corrected for temperature and atmospheric pressure and require thoroughly cleaned glassware, standard procedures for setting and reading the water meniscus, and accurate balances and thermometers.

Volumetric glassware is calibrated either "to contain" (TC) or "to deliver" (TD). Glassware designated as "to contain" has a mark referred to as the "fiducial mark." When the vessel is filled to that mark, it "contains" the designated volume. Emptying the vessel does not have any quantitative measure associated with it. "To deliver" glassware is not to be completely emptied or "blown out." Specified volumes for TD glassware do not include the residual left from surface adhesion and capillary action. TD glassware will perform with accuracy only when the inner surface is so scrupulously clean that the water wets it immediately and forms a uniform film when emptying.

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ATTACHMENT 18A
Control Charts

18A.1 Introduction

This attachment provides statistical details to augment Section 18.3.2. The term "statistical quality control" refers to QC based on statistical principles. Generally, statistical QC in the laboratory applies the principles of hypothesis testing, with varying degrees of rigor, to make inferences about a measurement system or process. The primary tool for statistical QC is the control chart.

An important reason to establish statistical QC in the laboratory is to ensure that measurement uncertainties are properly estimated. The uncertainty estimate that accompanies a measured value may be misleading unless the measurement process is in a state of *statistical control*. Statistical control implies that the distribution of measured results is stable and predictable. It exists when all the observed variability in the process is the result of random causes that are inherent in the process. The existence of variability due to "assignable" causes, including instrumental and procedural failures and human blunders, which are not inherent in the process, implies that the process is unpredictable and hence "out of control."

Statistical QC procedures are designed to detect variations due to assignable causes. When such variability is detected, specific corrective action is required to determine the cause and bring the measurement process back into a state of statistical control. Laboratory QC procedures should be definitive enough to detect variations in the measurement system that could have a significant impact on measurement uncertainties.

Statistical QC also may be used in the laboratory to monitor method performance parameters, such as chemical yield, to ensure that the measurement system is performing as expected. However, the need for corrective action in the case of a low yield may not be as urgent as in the case of a malfunctioning radiation counter, since the latter is much more likely to cause underestimation of measurement uncertainties.

The following sections describe the various types of control charts introduced in Section 18.3.2, including the X chart, $\overline{X}$ chart, R chart, and variants of the c chart and u chart for Poisson data.

18A.2 X Charts

Procedure 18.1, shown below, may be used to determine the central line, control limits, and warning limits for an X chart. Ideally, the data distribution should be approximately normal, although the X chart is often used with other types of distributions.

In order to use Procedure 18.1, an unbiased estimate of the standard deviation of the measured values $X_1, X_2, \ldots, X_n$ is required. Although the experimental variance s^2 of the data is an unbiased estimate of the true variance σ^2, taking the square root of s^2 generates a bias . The experimental standard deviation s is given by the equation

$$s = \sqrt{\frac{1}{n-1}\sum_{i=1}^{n}(X_i - \overline{X})^2} \tag{18.6}$$

If the data are (approximately) normally distributed, s should then be divided by a bias-correction factor, denoted by c_4, which is determined from the number of degrees of freedom, $\nu = n - 1$, as shown in Table 18A-1 below. Thus σ is estimated by s / c_4. The factor c_4 is defined as the ratio of the expected value of the experimental standard deviation, s, to the true standard deviation, σ, and can be shown to be equal to

$$c_4 = \frac{\Gamma\left(\frac{n}{2}\right)}{\Gamma\left(\frac{n-1}{2}\right)}\sqrt{\frac{2}{n-1}} \tag{18.7}$$

where Γ denotes the *gamma function* (NBS 1964), but it is well approximated by $c_4 \approx \frac{4n-4}{4n-3}$. For large n the value of c_4 is approximately 1.

TABLE 18A.1 — Bias-correction factor for the experimental standard deviation

$\nu = n - 1$	c_4	ν	c_4	ν	c_4	ν	c_4
1	0.79788	11	0.97756	21	0.98817	31	0.99197
2	0.88623	12	0.97941	22	0.98870	32	0.99222
3	0.92132	13	0.98097	23	0.98919	33	0.99245
4	0.93999	14	0.98232	24	0.98964	34	0.99268
5	0.95153	15	0.98348	25	0.99005	35	0.99288
6	0.95937	16	0.98451	26	0.99043	36	0.99308
7	0.96503	17	0.98541	27	0.99079	37	0.99327
8	0.96931	18	0.98621	28	0.99111	38	0.99344
9	0.97266	19	0.98693	29	0.99142	39	0.99361
10	0.97535	20	0.98758	30	0.99170	40	0.99377

An alternative method of estimating the standard deviation is based on the average value of the *moving range* (ASTM D6299, ASTM E882). The moving range (MR) is the absolute value of the difference between consecutive measured values X_i and X_{i+1}. If the data are normally distributed, the expected value of the moving range is

$$\frac{2\sigma}{\sqrt{\pi}} \approx 1.128\,\sigma \tag{18.8}$$

which may be estimated by

$$\overline{\mathrm{MR}} = \frac{1}{n-1}\sum_{i=1}^{n-1}\left|X_{i+1} - X_i\right| \tag{18.9}$$

So, σ is estimated by $\overline{\mathrm{MR}} / 1.128$. The moving-range estimate of σ may be preferred because it is less sensitive to outliers in the data. Furthermore, when consecutive values of X_i are correlated, as for example when a trend is present, the moving-range estimate may produce narrower control limits, which will tend to lead to earlier corrective action.

Procedure 18.1 (*X* chart). Determine the central line, control limits, and warning limits for an *X* chart based on a series of *n* independent measurements, which produce the measured values $X_1, X_2, \ldots, X_n$, during a period when the measurement process is in a state of statistical control. At least 2 measurements *must* be used. Ideally, at least 20 measurements should be used.

Procedure:

1. Calculate the sum $\Sigma_{i=1}^{n} X_i$
2. Calculate the arithmetic mean $\overline{X}$ using the formula

$$\overline{X} = \frac{1}{n}\sum_{i=1}^{n} X_i$$

3. Calculate an unbiased estimate $\overline{\sigma}$ of the standard deviation (e.g., s / c_4 or $\overline{\mathrm{MR}} / 1.128$)
4. Define the central line, control limits, and warning limits as follows:

$$\mathrm{CL} = \overline{X} \qquad \begin{array}{ll} \mathrm{UCL} = \overline{X} + 3\overline{\sigma} & \mathrm{LWL} = \overline{X} - 2\overline{\sigma} \\ \mathrm{LCL} = \overline{X} - 3\overline{\sigma} & \mathrm{UWL} = \overline{X} + 2\overline{\sigma} \end{array}$$

If *n* is less than 20, a higher rate of false warnings and failures may occur because of the increased uncertainties of the estimates $\overline{X}$ and $\overline{\sigma}$. So, fewer than 20 measured values should be used only if 20 values cannot be obtained; and the limits should be recalculated when 20 values become available.

EXAMPLE

Problem: Suppose a series of 20 observations of a parameter yield the following normally distributed values:

1,118.9	1,110.5	1,118.3	1,091.0	1,099.8	1,113.7	1,114.4	1,075.1	1,112.8	1,103.7
1,120.5	1,104.0	1,125.7	1,117.6	1,097.6	1,099.8	1,102.3	1,119.9	1,107.8	1,114.9

Determine the central line and warning and control limits for future measurements.

Solution:

Step 1 Calculate $\Sigma X_i = 22{,}168.3$

Step 2 Calculate the mean $\overline{X} = 22{,}168.3 / 20 = 1{,}108.415$

Step 3 Calculate the experimental standard deviation

$$s = \sqrt{\frac{1}{20 - 1}\sum_{i=1}^{20}(X_i - 1108.415)^2} = 12.044$$

which is based on $\nu = 19$ degrees of freedom. Find $c_4 = 0.98693$ for $\nu = 19$ in Table 18.1 (or estimate $c_4 \approx \frac{4n - 4}{4n - 3} = \frac{76}{77} = 0.9870$), and calculate

$$\overline{\sigma} = \frac{s}{c_4} = \frac{12.044}{0.98693} = 12.2037$$

Step 4 Define the central line, control limits, and warning limits as follows:

$$\begin{aligned} \text{CL} &= 1{,}108.415 \\ \text{UCL} &= 1{,}108.415 + 3(12.2037) = 1{,}145.0 \\ \text{LCL} &= 1{,}108.415 - 3(12.2037) = 1{,}071.8 \\ \text{UWL} &= 1{,}108.415 + 2(12.2037) = 1{,}132.8 \\ \text{LWL} &= 1{,}108.415 - 2(12.2037) = 1{,}084.0 \end{aligned}$$

18A.3 $\overline{X}$ Charts

When subgroup averages are plotted on a control chart, Steps 1 and 2 of Procedure 18.1 may be used to determine the arithmetic mean $\overline{X}$ and the standard deviation $\overline{\sigma}$ of a prior set of data $X_1, X_2, \ldots, X_n$. If k denotes the size of the subgroup, the central line, control limits, and warning limits for the subgroup average are calculated using the formulas

$$CL_{\overline{X}} = \overline{X} \qquad UCL_{\overline{X}} = \overline{X} + 3\overline{\sigma}/\sqrt{k} \qquad UWL_{\overline{X}} = \overline{X} + 2\overline{\sigma}/\sqrt{k}$$
$$LCL_{\overline{X}} = \overline{X} - 3\overline{\sigma}/\sqrt{k} \qquad LWL_{\overline{X}} = \overline{X} - 2\overline{\sigma}/\sqrt{k}$$

If n is less than about 20, a higher rate of false warnings and failures may occur because of the increased uncertainties of the estimates $\overline{X}$ and $\overline{\sigma}$. For this reason fewer than 20 measured values should be used only if 20 values cannot be obtained.

EXAMPLE

Problem: Use the data from the preceding example to determine warning and control limits for subgroup averages when the subgroup size is $k = 5$.

Solution:

Step 1 Calculate $\Sigma X_i = 22{,}168.3$

Step 2 Calculate the mean $\overline{X} = 22{,}168.3 / 20 = 1{,}108.415$

Step 3 Calculate the experimental standard deviation

$$s = \sqrt{\frac{1}{20 - 1}\sum_{i=1}^{20}(X_i - 1108.415)^2} = 12.044$$

which is based on $\nu = 19$ degrees of freedom. Find $c_4 = 0.98693$ for $\nu = 19$ in Table 18A-1 (or estimate $c_4 \approx \frac{4n-4}{4n-3} = \frac{76}{77} = 0.9870$), and calculate

$$\overline{\sigma} = \frac{s}{c_4} = \frac{12.044}{0.98693} = 12.2037$$

Step 4 Define the central line, control limits, and warning limits as follows:

$$CL_{\overline{X}} = 1{,}108.415$$
$$LCL_{\overline{X}} = 1{,}108.415 - 3(12.2037)/\sqrt{5} = 1{,}092.0$$
$$UCL_{\overline{X}} = 1{,}108.415 + 3(12.2037)/\sqrt{5} = 1{,}124.8$$
$$LWL_{\overline{X}} = 1{,}108.415 - 2(12.2037)/\sqrt{5} = 1{,}097.5$$
$$UWL_{\overline{X}} = 1{,}108.415 + 2(12.2037)/\sqrt{5} = 1{,}119.3$$

18A.4 *R* Charts

The *range* of a set of values is defined as the difference between the largest value and the smallest value in the set. When data are collected in subgroups, as described above, the range of each subgroup may be plotted on a *range chart*, or *R chart*, to monitor within-group variability.

The central line for an *R* chart can be obtained by averaging the observed ranges for a series of subgroups. Then the upper control limit for the chart can be obtained by multiplying the average range, $\overline{R}$, by a factor, denoted by D_4, whose value depends on the subgroup size, N. When $N \geq 7$, there is another factor, D_3, by which $\overline{R}$ can be multiplied to give the lower control limit. When $N < 7$, the *R* chart has no lower control limit. Values for D_3 and D_4 are tabulated in *Manual on Presentation of Data and Control Chart Analysis* (ASTM MNL7), as well as many other references.

For example, if an analyst makes a series of duplicate measurements of some quantity ($N = 2$), the central line of the *R* chart equals the average of the measured ranges, $\overline{R}$; the upper control limit equals the product of $\overline{R}$ and the factor D_4, whose value is 3.267 for duplicate measurements. The steps for calculating the central line and upper control limit when $N = 2$ are shown explicitly in Procedure 18.2 below.

Procedure 18.2 (*R* chart). Determine the central line and control limits for a *R* chart based on a series of n independent sets of duplicate measurements, which produce the values $R_1, R_2, \ldots, R_n$, during a period when the measurement process is in a state of statistical control.

Procedure:

1. Calculate the range, R_i, of each pair of duplicate measurements, (x_i, y_i)

$$R_i = |x_i - y_i|$$

2. Calculate the mean range, $\overline{R}$, using the formula

$$\overline{R} = \frac{1}{n} \sum_{i=1}^{n} R_i$$

3. Calculate the upper control limit as UCL = $3.267\ \overline{R}$

This approach may also be used for the moving range of a series of individual results.

EXAMPLE

Problem: Suppose a series of 20 duplicate observations of a parameter yield the following pairs of values.

(0.501, 0.491)	(0.490, 0.490)	(0.479, 0.482)	(0.520, 0.512)	(0.500, 0.490)
(0.510, 0.488)	(0.505, 0.500)	(0.475, 0.493)	(0.500, 0.515)	(0.498, 0.501)
(0.523, 0.516)	(0.500, 0.512)	(0.513, 0.503)	(0.512, 0.497)	(0.502, 0.500)
(0.506, 0.508)	(0.485, 0.503)	(0.484, 0.487)	(0.512, 0.495)	(0.509, 0.500)

Determine the central line and upper control limit for the range of future pairs of measurements.

Solution:

Step 1 Calculate the range of each of the 20 pairs:

0.010	0.000	0.003	0.008	0.010
0.022	0.005	0.018	0.015	0.003
0.007	0.012	0.010	0.015	0.002
0.002	0.018	0.003	0.017	0.009

Step 2 Calculate the mean range $\overline{R} = \frac{1}{20}\sum_{i=1}^{20} R_i = \frac{0.189}{20} = 0.00945$

Step 3 Calculate the upper control limit: UCL = 3.267 $\overline{R}$ = (3.267)(0.00945) = 0.0309

18A.5 Control Charts for Instrument Response

A radioactive check source should be used to monitor the radiation response/efficiency of every radiation counting instrument. MARLAP recommends that the activity and count time for the source be chosen to give no more than 1 percent counting uncertainty (ANSI N42.23). In other words, at least 10,000 counts should be obtained in each measurement of the source. There may be cases when placing a high-activity source in a detector is undesirable, so obtaining 10,000 counts is impractical.

The instrument response may not have a Poisson distribution. In this case, if the check source is long-lived, an X or $\overline{X}$ chart based on replicate measurements should be set up. For example, an X or $\overline{X}$ chart is the appropriate radiation response/efficiency chart for a high-purity germanium detector when the area of a specific photopeak is monitored, since the calculated size of the photopeak may have significant sources of uncertainty in addition to counting uncertainty. An X or $\overline{X}$ chart may be used even if the response is truly Poisson, since the Poisson distribution in this case is approximated well by a normal distribution, but slightly better warning and control limits are obtained by using the unique properties of the Poisson distribution.

Standard guidance documents recommend two types of control charts for Poisson data. A "*c* chart" typically is used in industrial quality control to monitor the number of manufacturing defects per item. A "*u* chart" is used to monitor the number of defects per unit "area of opportunity," when the area of opportunity may vary. Thus, the values plotted on a *c* chart are counts and those plotted on a *u* chart are count rates. The same two types of charts may be adapted for monitoring counts and count rates produced by a radioactive check source. When a *u* chart is used, the "area of opportunity" equals the product of the count time and the source decay factor. In radiation laboratories a variant of the *u* chart is more often used when the count time remains fixed but the decay factor changes during the time when the chart is in use.

Before using control limits derived from the Poisson model, one should use Procedure E1, described in Section 18B.2 of Attachment 18B, to confirm experimentally that the Poisson approximation is adequate and that any excess variance is relatively small at the expected count rate. Factors such as source position that may vary during routine QC measurements should be varied to the same degree during the experiment.

Calculation of warning and control limits using the Poisson model requires only a precise measurement of the source at a time when the instrument is operating properly at the time of calibration. The precision can be improved either by counting the source longer or by averaging several measurements. In principle both approaches should provide equally good estimates of the count rate; however, an advantage of the latter approach is that it can provide the data needed to detect excess variance (using Procedure E1).

Procedures 18.2 and 18.3, listed below, may be used to determine warning and control limits for measurements of a radioactive check source when the total count follows the Poisson model. Procedure 18.2 is for control charts and should be used only when the expected count in each measurement is the same, for example when the source is long-lived and all count durations are equal. Procedure 18.3, which implements an alternative to the *u* chart, may be used in all other cases.

Procedure 18.2 (Control chart for Poisson efficiency check data with constant mean). A check source is counted n times on an instrument, producing the measured counts $N_1, N_2, \ldots, N_n$. (Ideally, n is at least 20.) Determine control limits and warning limits for future measurements of the source count on the same instrument.

Procedure:

1. Estimate the central line by

$$\mathrm{CL} = \frac{1}{n}\sum_{i=1}^{n} N_i$$

and the standard deviation by

$$s = \sqrt{\text{CL}}$$

NOTE: The estimate s is biased, but the bias is negligible for the large number of counts typically obtained from a check source.

2. Define the control limits and warning limits (in counts) as follows:

$$\text{UCL} = \text{CL} + 3s \qquad \text{UWL} = \text{CL} + 2s$$
$$\text{LCL} = \text{CL} - 3s \qquad \text{LWL} = \text{CL} - 2s$$

If n is less than 20, a higher rate of false warnings and failures may occur because of the uncertainty in the estimate of the mean. So, fewer than 20 measurements should be used only if 20 measured values are not available.

Procedure 18.3 (Control chart for Poisson efficiency check data with variable mean). A check source is counted n times ($n \geq 1$) on an instrument, producing the measured counts N_1, N_2, …, N_n. (It is assumed that the background level is negligible when compared to the source count rate.) Let t_i denote the duration of the i^{th} measurement and d_i the decay factor [for example, $\exp(-\lambda(\Delta t + 0.5\,t_i))$]. Determine control limits and warning limits for a future measurement of the source count on the same instrument when the counting period is T and the decay factor is D.

Procedure:

1. Compute the sums $\sum_{i=1}^{n} N_i$ and $\sum_{i=1}^{n} t_i d_i$.
2. Estimate the mean decay-corrected count rate by

$$\hat{r} = \frac{\sum_{i=1}^{n} N_i}{\sum_{i=1}^{n} t_i d_i}$$

3. Estimate the central line by

$$\text{CL} = \hat{r}\,TD$$

and the standard deviation s by

$$s = \sqrt{\text{CL}}$$

4. Define the control limits and warning limits as follows:

$$\text{UCL} = \text{CL} + 3s \qquad \text{UWL} = \text{CL} + 2s$$
$$\text{LCL} = \text{CL} - 3s \qquad \text{LWL} = \text{CL} - 2s$$

If $\Sigma t_i d_i < 20\,TD$, a higher rate of false warnings and failures may occur because of increased uncertainty in the estimate of the count rate $\hat{r}$.

EXAMPLE

Problem: A source containing ^{90}Sr and ^{90}Y in equilibrium is used for efficiency checks on a proportional counter. Near the time of calibration, a series of twenty 600-s measurements are made. The observed counts are as follows:

12,262	12,561	12,606	12,381	12,394	12,518	12,399	12,556	12,565	12,444
12,432	12,723	12,514	12,389	12,383	12,492	12,521	12,619	12,397	12,562

Assume all twenty measurements are made approximately at time 0, so the ten decay factors d_i are all equal to 1. Use Procedure 18.3 to calculate lower and upper control limits for a 600-s measurement of the same source at a time exactly 1 year later.

Solution:

Step 1 Compute the sums $\Sigma N_i = 249{,}718$ and $\Sigma t_i d_i = 12{,}000$.

Step 2 Calculate $\hat{r} = \dfrac{\Sigma N_i}{\Sigma t_i d_i} = \dfrac{249{,}718}{12{,}000} = 20.80983$

Step 3 The decay time for the final measurement is 1 y = 31,557,600 s. The corresponding decay factor is $D = 0.976055$. The count time is $T = 600$ s. So, compute

$$\text{CL} = (20.80983)(600)(0.976055) = 12{,}187$$

and

$$s = \sqrt{12{,}187} = 110.39$$

Step 4 The control limits and warning limits are

$$\text{UCL} = 12{,}187 + 3 \times 110.39 = 12{,}518$$
$$\text{LCL} = 12{,}187 - 3 \times 110.39 = 11{,}856$$
$$\text{UWL} = 12{,}187 + 2 \times 110.39 = 12{,}408$$
$$\text{LWL} = 12{,}187 - 2 \times 110.39 = 11{,}966$$

If substantial excess (non-Poisson) variance is present in the data, the simple Poisson charts described above should not be used. The *c* chart may be replaced by an *X* chart or $\overline{X}$ chart, but a new type of chart is needed to replace the *u* chart. To determine warning and control limits for this chart, one must determine the relative excess variance of the data ξ^2. A value of ξ^2 may be assumed or it may be estimated using procedures described in Attachment 18B. Then Procedure 18.3 may be replaced by the Procedure 18.4, shown below.

Procedure 18.4 (Control chart for Poisson efficiency check data with excess variance). A check source is counted *n* times on an instrument, producing the measured counts $N_1, N_2, \ldots, N_n$. Let t_i denote the duration of the i^{th} measurement and d_i the decay factor. Let the data follow an approximately Poisson distribution with relative excess variance ξ^2. Determine control limits and warning limits for a future measurement of the source count on the same instrument when the counting period is *T* and the decay factor is *D*.

Procedure:

1. Compute the sums $\Sigma_{i=1}^{n} N_i$ and $\Sigma_{i=1}^{n} t_i d_i$
2. Estimate the mean decay-corrected count rate $\hat{r}$ by

$$\hat{r} = \frac{\displaystyle\sum_{i=1}^{n} \frac{N_i}{1 + r_0 t_i d_i \xi^2}}{\displaystyle\sum_{i=1}^{n} \frac{1}{1 + r_0 t_i d_i \xi^2}} \qquad \text{where} \qquad r_0 = \frac{\Sigma_{i=1}^{n} N_i}{\Sigma_{i=1}^{n} t_i d_i}$$

3. Estimate the central line by

$$\text{CL} = \hat{r} TD$$

and the standard deviation *s* by

$$s = \sqrt{\text{CL} + \xi^2 \text{CL}^2}$$

4. Define the control limits and warning limits as follows:

$$\text{UCL} = \text{CL} + 3s \qquad \text{UWL} = \text{CL} + 2s$$
$$\text{LCL} = \text{CL} - 3s \qquad \text{LWL} = \text{CL} - 2s$$

18A.6 References

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ATTACHMENT 18B
Statistical Tests for QC Results

18B.1 Introduction

Attachment 18A describes several types of control charts that may be used for statistical quality control in the laboratory. This attachment describes additional statistical methods that may be used, where appropriate, to test the performance of measurement results from blank, replicate, LCS, spikes, CRM, yield-monitor, background, efficiency, calibration, or peak resolution results, with special emphasis on instrumentation results.

18B.2 Tests for Excess Variance in the Instrument Response

As noted in Chapter 19, the counting uncertainty given by the Poisson approximation does not describe the total variability in a counting measurement. A number of factors may generate a small excess component of variance. When a large number of counts are obtained in the measurement, the relative magnitude of the Poisson variance is small; so, the excess component may dominate.

Regardless of whether replication or the Poisson approximation is used to estimate counting uncertainties, MARLAP recommends that a series of check source measurements be made on each instrument periodically to test for excess variance. Procedure E1, which is presented below, may be used to evaluate the measurement results. To check the stability of the instrument itself, one should perform the measurements while holding constant any controllable factors, such as source position, that might increase the variance. To check the variance when such factors are not constant, one may use Procedure E1 but vary the factors randomly for each measurement.

Assume n measurements of the source produce the counts $N_1, N_2, \ldots, N_n$. If the expected count for each measurement is at least 20, so that the Poisson distribution is approximated by a normal distribution, and if the average decay-corrected count rate $\hat{r}$ is determined with adequate precision, then the quantity

$$\chi^2 = \frac{1}{\hat{r}} \sum_{i=1}^{n} \left(\frac{N_i}{t_i d_i} - \hat{r} \right)^2 t_i d_i \qquad (18.10)$$

where t_i and d_i are the count time and source decay factor for the i^{th} measurement, respectively, should be distributed approximately as chi-square with $n - 1$ degrees of freedom.[5] The precision

[5] If r denotes the true mean decay-corrected count rate, then under the null hypothesis each measured count rate $N_i / t_i d_i$ is approximately normal with mean r and variance $r / t_i d_i$, and the least-squares estimator for r is $\hat{r} = \Sigma N_i / \Sigma t_i d_i$. So, the sum $\Sigma (N_i / t_i d_i - \hat{r})^2 / (r / t_i d_i)$ is approximately chi-square with $n - 1$ degrees of freedom.

of the estimate $\hat{r}$ should be adequate for the test as long as the expected count for each measurement is at least 20. Since a check source is involved, the expected count is usually much greater than 20.

Procedure E1. The χ^2 (chi-square) analysis can be used to determine whether a series of measurements of a check source provide evidence of variance in excess of the Poisson counting variance. Let N_i denote the count observed in the i^{th} measurement. Let $w_i = t_i d_i$, where t_i denotes the count time and d_i denotes the source decay factor (if relevant). If all the values w_i are equal, one may use $w_i = 1$ instead for all i. It is assumed either that the background count rate is negligible or that the decay factors are all nearly equal, so that the expected count in each measurement is proportional to w_i.[6] The procedure tests the null hypothesis that the total measurement variance is the Poisson counting variance.

Procedure:

1. Choose the significance level α
2. Calculate the sums $\Sigma_{i=1}^{n} N_i$ and $\Sigma_{i=1}^{n} w_i$
3. Estimate the mean decay-corrected count rate by

$$\hat{r} = \frac{\Sigma_{i=1}^{n} N_i}{\Sigma_{i=1}^{n} w_i} \tag{18.11}$$

4. Calculate the chi-square statistic as follows:

$$\chi^2 = \frac{1}{\hat{r}} \sum_{i=1}^{n} \left(\frac{N_i}{w_i} - \hat{r} \right)^2 w_i \tag{18.12}$$

5. Determine the quantile $\chi^2_{1-\alpha}(n-1)$ (see Table G.3 in Appendix G). Reject the null hypothesis if and only if the calculated value of χ^2 is greater than $\chi^2_{1-\alpha}(n-1)$. In this case conclude that the variance is greater than predicted by the Poisson model.

If $\hat{r}$ is determined accurately, the true mean count rate r may be replaced in the formula by its estimated value $\hat{r}$ to obtain the formula that appears in the text. If all the products $t_i d_i$ are equal, they cancel out of the sum, which becomes $\Sigma (N_i - \overline{N})^2 / \overline{N}$, as described by Evans (1955), Goldin (1984), and Knoll (1989).

[6] The expected gross count for the i^{th} measurement equals $R_B t_i + r w_i$, where r is the mean net count rate at time 0. The expected count is proportional to w_i if $R_B = 0$, or if all the decay factors are equal so that $t_i \propto w_i$.

EXAMPLE

Problem: A long-lived source is counted $n = 20$ times in a gross radiation detector and the duration of each measurement is 300 s. The following total counts are measured:

11,189	11,105	11,183	10,910	10,998	11,137	11,144	10,751	11,128	11,037
11,205	11,040	11,257	11,176	10,976	10,998	11,023	11,199	11,078	11,149

Are these data consistent with the assumption that the measurement variance is no greater than predicted by the Poisson model? Use 5 percent as the significance level.

Solution:

Step 1 The significance level is specified to be $\alpha = 0.05$

Step 2 Since the source is long-lived and all the count times are equal, let $w_i = 1$ for each i. Calculate $\Sigma N_i = 221{,}683$ and $\Sigma w_i = 20$

Step 3 Calculate the mean count rate $\hat{r} = 221{,}683 / 20 = 11{,}084.15$

Step 4 Calculate the chi-square statistic

$$\chi^2 = \frac{1}{\hat{r}} \sum_{i=1}^{n} \left(\frac{N_i}{w_i} - \hat{r} \right)^2 w_i = \frac{1}{11{,}084.15} \sum_{i=1}^{20} (N_i - 11{,}084.15)^2 = 24.87$$

Step 5 The number of degrees of freedom is $20 - 1 = 19$. According to Table G.3, the 0.95-quantile for a chi-square distribution with 19 degrees of freedom is 30.14. Since $24.87 \leq 30.14$, do not reject the null hypothesis. The data are consistent with the assumption of Poisson counting statistics at the 5 percent significance level.

A two-sided version of Procedure E1 may also be used to test whether the measurement variance is either greater than or less than predicted by the Poisson model. Step 5 must be changed so that the null hypothesis is rejected if the value of the test statistic χ^2 does not lie between the two quantiles $\chi^2_{\alpha/2}(n - 1)$ and $\chi^2_{1-\alpha/2}(n - 1)$.

A chi-square test may require many measurements or long count times to detect a small excess variance component. When all measurements have the same expected count μ, the detection limit for the *relative* excess variance, or its minimum detectable value, is equal to

$$\xi^2_D = \frac{1}{\mu} \left(\frac{\chi^2_{1-\alpha}(n - 1)}{\chi^2_{\beta}(n - 1)} - 1 \right) \tag{18.13}$$

where β is the specified probability of a type II error (failure to detect) (Currie,1972). Note that since ξ_D^2 represents a relative variance, its square root ξ_D represents a relative standard deviation.

EXAMPLE: A long-lived source is counted 20 times, and each measurement has the same duration. The average of the measured counts is 10,816. If $\alpha = \beta = 0.05$, the minimum detectable value of the relative excess variance is estimated by

$$\xi_D^2 = \frac{1}{10{,}816}\left(\frac{\chi^2_{0.95}(19)}{\chi^2_{0.05}(19)} - 1\right) = \frac{1}{10{,}816}\left(\frac{30.14}{10.12} - 1\right) = \frac{1.978}{10{,}816} = 1.829 \times 10^{-4}$$

which corresponds to a relative standard deviation $\xi_D = \sqrt{1.829 \times 10^{-4}} = 0.01352$, or about 1.35 percent.

If (1) the relative excess variance in a measurement is not affected by count time, (2) a fixed total count time is available, and (3) all measurements have the same expected count (e.g., when all count times are equal and the source is long-lived), then it is possible to determine the number of measurements that minimizes ξ_D^2 (Currie, 1972). The optimal number is the number n that minimizes the quantity

$$F(n) = n\left(\frac{\chi^2_{1-\alpha}(n-1)}{\chi^2_{\beta}(n-1)} - 1\right) \tag{18.14}$$

The solution may be found by computing $F(n)$ for $n = 2, 3, 4, \ldots$, until the computed value begins to increase. When $\alpha = \beta = 0.05$, the optimal number of measurements is $n = 15$, although the improvement as n increases from 6 to 15 is slight. If n is increased further, the detection limit ξ_D^2 worsens unless the total count time is also increased.

A chi-square test may also be used to test whether the total source measurement variance consists of a Poisson component and a specified excess component (Currie 1972). Procedure E2, described below, implements this test. If the specified component is zero, Procedure E2 is equivalent to E1.

Procedure E2. Determine whether a series of measurements of a check source provide evidence that the measurement variance is greater than the Poisson component plus a specified excess component. (Refer to the notation used in Procedure E1.) Let ξ^2 denote the value of the relative excess variance under the null hypothesis H_0.

Procedure:

1. Choose the significance level α.

2. Calculate the sums $\sum_{i=1}^{n} N_i$ and $\sum_{i=1}^{n} w_i$, where $N_1, N_2, \ldots, N_n$ are the measured values.

3. Estimate the mean decay-corrected count rate $\hat{r}$ in two steps by

$$r_0 = \frac{\sum_{i=1}^{n} N_i}{\sum_{i=1}^{n} w_i} \qquad \text{and} \qquad \hat{r} = \sum_{i=1}^{n} \frac{N_i}{1 + r_0 w_i \xi^2} \Big/ \sum_{i=1}^{n} \frac{w_i}{1 + r_0 w_i \xi^2} \tag{18.15}$$

   (If $w_1 = w_2 = \cdots = w_n$ or $\xi^2 = 0$, then $\hat{r} = r_0$.)

4. Calculate the chi-square statistic as follows:[7]

$$\chi^2 = \sum_{i=1}^{n} \frac{(N_i / w_i - \hat{r})^2}{\hat{r} / w_i + \hat{r}^2 \xi^2} \tag{18.16}$$

5. Determine the quantile $\chi^2_{1-\alpha}(n-1)$ (see Table G.3). Reject the null hypothesis if and only if the calculated value of χ^2 is greater than $\chi^2_{1-\alpha}(n-1)$. In this case conclude that the relative excess variance is greater than ξ^2.

Procedure E2, like E1, can easily be converted to a two-sided test by changing Step 5.

The excess component may be estimated by solving Equations 18.15 and 18.16 for the value of ξ that gives $\chi^2 = n - 1$. An iterative computer algorithm, such as bisection, which repeatedly tries values of ξ and computes χ^2 can be used.[8] An approximate confidence interval for the relative excess variance may similarly be found by solving for values of ξ which give $\chi^2 = \chi^2_{(1\pm\gamma)/2}(n-1)$, where γ is the desired confidence coefficient (Currie, 1972).

If $w_1 = w_2 = \cdots = w_n$, the iterative algorithm is unnecessary. In this case the value of ξ may be estimated directly using the formula

[7] In Currie (1972), the variance of N_i is estimated by $N_i + \xi^2 N_i^2$. The estimated variance used here is calculated by pooling the counting data to reduce any small bias caused by the correlation between N_i and $N_i + \xi^2 N_i^2$.

[8] Newton's method, which converges more rapidly, can also be used, but its use is more practical if one replaces $\hat{r}$ by r_0 in the denominator of each term of Equation 18.16.

$$\xi^2 = \frac{1}{\overline{N}^2}\left(\frac{1}{n-1}\sum_{i=1}^{n}(N_i - \overline{N})^2 - \overline{N}\right) \tag{18.17}$$

or by $\xi = 0$ if the preceding formula gives a negative result. Similarly, the approximate lower confidence limit is given by the formula

$$\xi^2_{\text{lower}} = \frac{1}{\overline{N}^2}\left(\frac{1}{\chi^2_{(1+\gamma)/2}(n-1)}\sum_{i=1}^{n}(N_i - \overline{N})^2 - \overline{N}\right) \tag{18.18}$$

and the approximate upper confidence limit is given by

$$\xi^2_{\text{upper}} = \frac{1}{\overline{N}^2}\left(\frac{1}{\chi^2_{(1-\gamma)/2}(n-1)}\sum_{i=1}^{n}(N_i - \overline{N})^2 - \overline{N}\right) \tag{18.19}$$

EXAMPLE

Problem: A long-lived efficiency check source is counted once a day for 20 days, and each measurement has the same duration. Suppose the measured counts (N_i) are:

14,454	15,140	15,242	14,728	14,756	15,040	14,768	15,128	15,150	14,872
14,845	15,511	15,032	14,746	14,731	14,982	15,047	15,272	14,765	15,143

Use these data to estimate ξ and determine a 95 percent two-sided confidence interval for its value.

Solution: Since the source is long-lived and all the measurements have the same duration, $w_1 = w_2 = \cdots = w_{20}$ and Equations 18.17 through 18.19 may be used. So, calculate $\Sigma N_i = 299{,}352$ and $\overline{N} = 299{,}352 / 20 = 14{,}967.6$. Then the value of ξ is estimated as

$$\xi = \frac{1}{14{,}967.6}\sqrt{\frac{1}{20-1}\sum_{i=1}^{20}(N_i - 14{,}967.6)^2 - 14{,}967.6} = 0.014463$$

The 95 percent confidence limits are calculated as follows:

$$\xi_{\text{lower}} = \frac{1}{\overline{N}}\sqrt{\frac{1}{\chi^2_{0.975}(20-1)}\sum_{i=1}^{20}(N_i - \overline{N})^2} - \overline{N}$$

$$= \frac{1}{14{,}967.6}\sqrt{\frac{1}{32.852}\sum_{i=1}^{20}(N_i - 14{,}967.6)^2} - 14{,}967.6$$

$$= 0.0096334$$

$$\xi_{\text{upper}} = \frac{1}{\overline{N}}\sqrt{\frac{1}{\chi^2_{0.025}(20-1)}\sum_{i=1}^{20}(N_i - \overline{N})^2} - \overline{N}$$

$$= \frac{1}{14{,}967.6}\sqrt{\frac{1}{8.9065}\sum_{i=1}^{20}(N_i - 14{,}967.6)^2} - 14{,}967.6$$

$$= 0.022846$$

For most practical purposes the excess variance may be considered negligible in a counting measurement if the total count N is less than $1 / 10\xi^2$, since, in this case, the excess variance increases the standard deviation of the measured count by less then 5 percent. Similarly, the counting variance may be considered negligible if $N \geq 10 / \xi^2$.

EXAMPLE: Suppose $N = 1{,}000$ counts observed in a measurement and ξ has been estimated to be 0.01. Then $N = 1 / 10\xi^2$. The standard uncertainty of N is evaluated as

$$u(N) = \sqrt{N + \xi^2 N^2} = \sqrt{1{,}000 + 10^{-4}10^6} = \sqrt{1{,}100} \approx 1.05\sqrt{N}$$

If $N = 100{,}000$, then $N = 10 / \xi^2$ and

$$u(N) = \sqrt{10^5 + 10^{-4}10^{10}} = \sqrt{1{,}100{,}000} \approx 1.05(\xi N)$$

So, $u(N) \approx \sqrt{N}$ for $N \leq 1{,}000$, and $u(N) \approx \xi N$ for $N \geq 100{,}000$.

18B.3 Instrument Background Measurements

This section presents statistical tests related to measurements of instrument background levels. The tests are intended for single-channel detectors but may be applied to multichannel systems if wide spectral regions are integrated. Tests are described for comparing background levels to preset limits, for detecting changes in background levels between measurements, and for detecting the presence of variability in excess of that predicted by the Poisson model.

Each of the statistical tests in this section includes different instructions depending on whether the number of background counts in a measurement is at least 20. The reason for this is that when the expected number of counts is high enough, the Poisson distribution can be approximated by a normal distribution, which simplifies the test procedure. For more information about the Poisson distribution and the normal approximation, see Section 19A.2.9, "Poisson Distributions."

18B.3.1 Detection of Background Variability

The chi-square test (Procedure E1) used to detect excess variance in measurements of a check source may be adapted for background measurements. Procedure B1 implements a chi-square test for backgrounds. This test is one-sided, although Step 6 can be modified to implement a two-sided test.

Procedure B1. Determine whether a series of measurements of an instrument's background provide evidence of variance in excess of the Poisson counting variance. Let N_i denote the count observed in the i^{th} measurement, and let t_i denote the count time.

Procedure:

1. Determine the significance level α
2. Calculate the sums $\Sigma_{i=1}^{n} N_i$ and $\Sigma_{i=1}^{n} t_i$
3. Estimate the mean background count rate by

$$\hat{r} = \frac{\Sigma_{i=1}^{n} N_i}{\Sigma_{i=1}^{n} t_i} \tag{18.20}$$

4. Let $t_{\min}$ be the smallest value of t_i. If $\hat{r} t_{\min} \geq 20$, go to Step 5. Otherwise, discard all measured values N_i for which $\hat{r} t_i < 20$. If possible, restart the test at Step 2; if not, stop.

5. Calculate the chi-square statistic as follows:

$$\chi^2 = \frac{1}{\hat{r}} \sum_{i=1}^{n} \left(\frac{N_i}{t_i} - \hat{r} \right)^2 t_i \qquad (18.21)$$

6. Determine the quantile $\chi^2_{1-\alpha}(n-1)$ (see Table G.3 in Appendix G). Reject the null hypothesis if and only if the calculated value of χ^2 is greater than $\chi^2_{1-\alpha}(n-1)$. In this case, conclude that the instrument background does not follow the Poisson model.

EXAMPLE

Problem: Twenty overnight background measurements are performed on a proportional counter. The duration of each measurement is 60,000 s, and the following alpha counts are measured:

14	23	23	25	28	22	19	26	20	27
30	21	34	32	24	27	25	19	19	25

Are these data consistent with the assumption that the measurement variance is attributable to Poisson counting statistics? Use 5 percent as the significance level.

Solution:

Step 1 The significance level is specified to be $\alpha = 0.05$

Step 2 Calculate $\Sigma N_i = 483$ and $\Sigma t_i = 20 \times 60{,}000 = 1{,}200{,}000$

Step 3 Calculate the mean count rate $\hat{r} = 483 / 1{,}200{,}000 = 0.0004025$

Step 4 Since $t_{\min} = 60{,}000$, $\hat{r}t_{\min} = 24.15$. Since $24.15 \geq 20$, go to Step 5

Step 5 Calculate the chi-square statistic

$$\chi^2 = \frac{1}{\hat{r}} \sum_{i=1}^{n} \left(\frac{N_i}{t_i} - \hat{r} \right)^2 t_i = \frac{1}{0.0004025} \sum_{i=1}^{20} \left(\frac{N_i}{60{,}000} - 0.0004025 \right)^2 60{,}000 = 18.49$$

Step 6 The number of degrees of freedom is $20 - 1 = 19$. According to Table G.3, the 0.95-quantile for a chi-square distribution with 19 degrees of freedom is 30.14. Since $18.49 \leq 30.14$, do not reject the null hypothesis. The data are consistent with the Poisson model.

All the background tests described below are based on the assumption of Poisson counting statistics. If Procedure B1 indicates the Poisson assumption is invalid, each test requires modification or replacement. In most cases, unless the observed background counts are very low, standard statistical tests for normally distributed data may be used instead (e.g., NBS, 1963; EPA, 2000).

18B.3.2 Comparing a Single Observation to Preset Limits

High background levels on an instrument degrade detection capabilities and may indicate the presence of contamination. Unusually low levels on certain types of instruments may indicate instrument failure. When these issues are of concern, one or both of the two statistical tests described below may be performed to determine whether the true background level is outside of its desired range.

The result of the background measurement in counts is assumed to have a Poisson distribution. In both of the following tests, t denotes the count time, and r denotes the preset lower or upper limit for the true mean background count rate R_B. Given an observed count N_B, Procedure B2 determines whether $R_B > r$ and B3 determines whether $R_B < r$.

Procedure B2 should be used when r is an upper limit and B3 should be used when r is a lower limit. Thus, the background level is assumed to be within its acceptable limits unless there is statistical evidence to the contrary. The alternative approach, which changes the burden of proof, may be used if rt is large enough.

If rt is extremely large (e.g., if $rt \geq 2{,}500$), there is probably no justification for a statistical test. Instead, the observed count rate may be compared directly to r.

Procedure B2. Determine whether the mean background count rate R_B is greater than r. Test the null hypothesis H_0: $R_B \leq r$ against the alternative hypothesis H_1: $R_B > r$.

Procedure:

1. Choose the significance level α.

2. If $N_B \leq rt$, conclude that there is insufficient evidence to reject the null hypothesis, and stop. Otherwise, if $rt < 20$, go to Step 6. If $rt \geq 20$, go to Step 3.

3. Calculate

$$Z = \frac{0.5 + N_B - rt}{\sqrt{rt}} \tag{18.22}$$

4. Determine $z_{1-\alpha}$, the $(1-\alpha)$-quantile of the standard normal distribution (see Table G.1 in Appendix G).

5. Reject the null hypothesis if and only if $Z > z_{1-\alpha}$. Stop.

NOTE: If the background count time t is always the same, a fixed upper control limit may be calculated using the formula

$$\text{UCL} = \textbf{round}\left(rt + z_{1-\alpha}\sqrt{rt}\right)$$

where **round** denotes the function that rounds its argument to the nearest integer. Then Steps 3–5 are effectively performed by comparing the observed value N_B to UCL.

6. Determine $\chi^2_\alpha(2N_B)$, the α-quantile of the chi-square distribution with $2N_B$ degrees of freedom (see Table G.3 in Appendix G), and calculate $Q = 0.5\,\chi^2_\alpha(2N_B)$.

7. Reject the null hypothesis if and only if $Q > rt$.

EXAMPLE

Problem: To ensure adequate detection capabilities, a laboratory establishes an upper limit of 0.02 cps for beta backgrounds on a proportional counter. A 6,000-s background measurement is performed, during which 125 beta counts are observed. Determine whether this measurement result gives 95 percent confidence that the background is greater than 0.02 cps.

Solution:	The values of the variables are $N_B = 125$, $t = 6{,}000$ and $r = 0.02$
Step 1	The significance level α is $1 - 0.95 = 0.05$
Step 2	Since $N_B \geq rt = 120$ and $rt \geq 20$, go to Step 3
Step 3	Calculate $Z = (0.5 + 125 - 120) / \sqrt{120} = 0.5021$
Step 4	Table G.1 shows that $z_{0.95} = 1.645$
Step 5	Since $0.5021 \leq 1.645$, do not reject the null hypothesis. There is insufficient evidence to conclude that the beta background exceeds 0.02 cps

EXAMPLE

Problem: The same laboratory establishes an upper limit of 0.002 cps for alpha backgrounds on the same counter. A 6,000-s background measurement is performed, during which 19 alpha counts are observed. Determine whether this measurement result gives 95 percent confidence that the background is greater than 0.002 cps.

Solution:	The values of the variables are $N_B = 19$, $t = 6{,}000$ and $r = 0.002$
Step 1	The significance level α is $1 - 0.95 = 0.05$
Step 2	Since $N_B \geq rt = 12$ and $rt < 20$, go to Step 6

Step 6	Table G.3 shows that $\chi^2_{0.05}(38) = 24.88$. So, $Q = 0.5 \cdot 24.88 = 12.44$
Step 7	Since 12.44 > 12, reject the null hypothesis. The data give 95 percent confidence that the alpha background is greater than 0.002 cps.

Procedure B3. Determine whether the mean background count rate R_B is less than r. Test the null hypothesis H_0: $R_B \geq r$ against the alternative hypothesis H_1: $R_B < r$.

Procedure:

1. Choose the significance level α.

2. If $N_B \geq rt$, conclude that there is insufficient evidence to reject the null hypothesis, and stop. Otherwise, if $rt < 20$, go to Step 6. If $rt \geq 20$, go to Step 3.

3. Calculate

$$Z = \frac{0.5 + N_B - rt}{\sqrt{rt}} \tag{18.23}$$

4. Determine $z_{1-\alpha}$, the $(1-\alpha)$-quantile of the standard normal distribution (see Table G.1 in Appendix G).

5. Reject the null hypothesis if and only if $Z < -z_{1-\alpha}$. Stop.

   NOTE: If the background count time t is always the same, a lower control limit may be calculated using the formula

   $$\text{LCL} = \textbf{round}\left(rt - z_{1-\alpha}\sqrt{rt}\right).$$

   Steps 3–5 are then effectively performed by comparing N_B to LCL.

6. Determine $\chi^2_{1-\alpha}(2N_B + 2)$, the $(1-\alpha)$-quantile of the chi-square distribution with $2N_B + 2$ degrees of freedom (see Table G.3), and calculate $Q = 0.5\,\chi^2_{1-\alpha}(2N_B + 2)$.

7. Reject the null hypothesis if and only if $Q < rt$.

EXAMPLE

Problem: A laboratory establishes a lower limit of 0.01 cps for beta backgrounds on a proportional counter. A 6,000-s background measurement is performed, during which 50 beta counts are observed. Determine whether this measurement result gives 95 percent confidence that the background is less than 0.01 cps.

Solution:	The values of the variables are $N_B = 50$, $t = 6{,}000$ and $r = 0.01$
Step 1	The significance level α is $1 - 0.95 = 0.05$
Step 2	Since $N_B \leq rt = 60$ and $rt \geq 20$, go to Step 3
Step 3	Calculate $Z = (0.5 + 50 - 60) / \sqrt{60} = -1.226$
Step 4	Table G.1 shows that $z_{0.95} = 1.645$
Step 5	Since $-1.226 \geq -1.645$, do not reject the null hypothesis.

18B.3.3 Comparing the Results of Consecutive Measurements

If consecutive measurements of the background level on an instrument give significantly different values, one should be concerned about the accuracy of any laboratory sample measurements made between the two background measurements. If the background has increased, the laboratory sample activities may have been overestimated. If the background has decreased, the activities may have been underestimated. For very low background applications, when the number of observed counts per measurement approaches zero (as encountered in alpha spectrometry), the tests for comparing statistical equivalence of paired backgrounds can be confounded. In these cases, it may be better to examine populations of blanks with $N \geq 20$.

Let N_1 and N_2 denote the counts observed in two independent background measurements on the same instrument, and assume they represent Poisson distributions with unknown means. Let t_1 and t_2 denote the corresponding count times. The following two procedures may be used to determine whether the difference between the two observed values is significantly larger than would be expected on the basis of the Poisson model. Procedure B4 determines whether the second value is significantly greater than the first. Procedure B5 determines whether there is a significant difference between the two values.

Procedure B4. Determine whether the second mean background count rate R_2 is higher than the first R_1. Test the null hypothesis H_0: $R_1 \geq R_2$ against the alternative hypothesis H_1: $R_1 < R_2$.

Procedure:

1. Choose the significance level α.

2. If $N_1 / t_1 \geq N_2 / t_2$, conclude that there is insufficient evidence to reject the null hypothesis, and stop. Otherwise, if $N_1 \geq 20$ and $N_2 \geq 20$, go to Step 3. If $N_1 < 20$ or $N_2 < 20$, go to Step 6.

3. Calculate

$$Z = \left(\frac{N_2}{t_2} - \frac{N_1}{t_1} \right) \Bigg/ \sqrt{\frac{N_1 + N_2}{t_1 t_2}} \tag{18.24}$$

4. Determine $z_{1-\alpha}$, the $(1 - \alpha)$-quantile of the standard normal distribution.

5. Reject the null hypothesis if and only if $Z > z_{1-\alpha}$. Stop.

6. Let $p = t_1 / (t_1 + t_2)$ and $q = t_2 / (t_1 + t_2)$. If $N_1 < N_2$, calculate

$$S = \sum_{k=0}^{N_1} \binom{N_1 + N_2}{k} p^k q^{N_1 + N_2 - k} \tag{18.25}$$

If $N_1 \geq N_2$, calculate S more efficiently using the formula

$$S = 1 - \sum_{k=N_1+1}^{N_1+N_2} \binom{N_1 + N_2}{k} p^k q^{N_1 + N_2 - k} \tag{18.26}$$

NOTE: For any nonnegative integers n and k, the notation $\binom{n}{k}$ denotes a *binomial coefficient*, usually read "n choose k," which is the number of possible combinations of n objects chosen k at a time. For example, $\binom{4}{1} = 4$, $\binom{4}{2} = 6$, $\binom{4}{3} = 4$, and $\binom{4}{4} = 1$. In general, for $0 \leq k \leq n$, the value of $\binom{n}{k}$ equals $\frac{n!}{k!(n-k)!}$, where the symbol ! denotes the "factorial" operator. The number of combinations of n objects chosen k at a time is also denoted sometimes by ${}_nC_k$.

7. Reject the null hypothesis if and only if $S \leq \alpha$.

EXAMPLE

Problem: A 60,000-s background measurement is performed on an alpha spectrometer and 15 total counts are observed in a particular region of interest. After a test source is counted, a 6,000-s background measurement is performed and 3 counts are observed. Assuming Poisson counting statistics, is the second measured count rate (0.0005 cps) significantly higher than the first (0.00025 cps) at the 5 percent significance level?

Solution: The variables are $N_1 = 15$, $t_1 = 60{,}000$, $N_2 = 3$, and $t_2 = 6{,}000$

Step 1 The significance level α is specified to be 0.05

Step 2 Since $N_1 / t_1 = 0.00025 < 0.0005 = N_2 / t_2$, $N_1 < 20$, and $N_2 < 20$, go to Step 6

Step 6 $p = \frac{60{,}000}{66{,}000} = \frac{10}{11}$ and $q = \frac{6{,}000}{66{,}000} = \frac{1}{11}$. Since $N_1 \geq N_2$, calculate S using the second formula.

$$S = 1 - \left(\binom{18}{16} \left(\frac{10}{11}\right)^{16} \left(\frac{1}{11}\right)^{2} + \binom{18}{17} \left(\frac{10}{11}\right)^{17} \left(\frac{1}{11}\right)^{1} + \binom{18}{18} \left(\frac{10}{11}\right)^{18} \left(\frac{1}{11}\right)^{0} \right)$$

$$= 1 - 0.7788 = 0.2212 .$$

Step 7 Since $S \geq \alpha$, there is not enough evidence to reject the null hypothesis. The second measured count rate is not significantly higher than the first.

Procedure B5. Determine whether the mean background count rates are different. Test the null hypothesis H_0: $R_1 = R_2$ against the alternative hypothesis H_1: $R_1 \neq R_2$.

Procedure:

1. Choose the significance level α.

2. If $N_1 / t_1 = N_2 / t_2$, conclude that there is insufficient evidence to reject the null hypothesis, and stop. Otherwise, if $N_1 < 20$ or $N_2 < 20$, go to Step 6. If $N_1 \geq 20$ and $N_2 \geq 20$, go to Step 3.

3. Calculate Z using Equation 18.24.

4. Determine $z_{1-\alpha/2}$, the $(1 - \alpha / 2)$-quantile of the standard normal distribution.

5. Reject the null hypothesis if and only if $|Z| > z_{1-\alpha/2}$. Stop.

6. If $N_1 / t_1 < N_2 / t_2$, use Procedure B4 with significance level $\alpha / 2$ to determine whether $R_1 < R_2$. If $N_1 / t_1 > N_2 / t_2$, use Procedure B4 with significance level $\alpha / 2$ and with the observations reversed to determine whether $R_2 < R_1$.

18B.4 Negative Activities

When the measured count rate for a test source is less than that of the corresponding instrument background, giving a negative value for the source activity, Procedure B4 may be used to determine whether the difference between the two count rates is significantly more than should be expected on the basis of the Poisson model and the assumption that the source is a blank. (Let N_1 and t_1 be the source count and counting time and let N_2 and t_2 be the background count and counting time.). If a significant difference is found, it may indicate that the background measurement was biased, the true background is variable or non-Poisson, or the instrument is unstable. As background counts approach zero, the assumption of Poisson statistics begins to fail. This mean-centered approach may lead the analyst to an inappropriate conclusion. In these cases, an examination of a larger population of blanks is more appropriate.

18B.5 References

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19 MEASUREMENT UNCERTAINTY

19.1 Overview

This chapter discusses the evaluation and reporting of measurement uncertainty. Laboratory measurements always involve uncertainty, which must be considered when analytical results are used as part of a basis for making decisions.[1] Every measured result reported by a laboratory should be accompanied by an explicit uncertainty estimate. One purpose of this chapter is to give users of radioanalytical data an understanding of the causes of measurement uncertainty and of the meaning of uncertainty statements in laboratory reports. The chapter also describes procedures which laboratory personnel use to estimate uncertainties.

This chapter has more than one intended audience. *Not all readers are expected to have the mathematical skills necessary to read and completely understand the entire chapter*. For this reason the material is arranged so that general information is presented first and the more technical information, which is intended primarily for laboratory personnel with the required mathematical skills, is presented last. The general discussion in Sections 19.2 and 19.3 requires little previous knowledge of statistical metrology on the part of the reader and involves no mathematical formulas; however, if the reader is unfamiliar with the fundamental concepts and terms of probability and statistics, he or she should read Attachment 19A before starting Section 19.3. The technical discussion in Sections 19.4 and 19.5 requires an understanding of basic algebra and at least some familiarity with the fundamental concepts of probability and statistics. The discussion of uncertainty propagation requires knowledge of differential calculus for a complete understanding. Attachments 19C–E are intended for technical specialists.

The major recommendations of the chapter are summarized in Section 19.3.9.

Contents

19.2 The Need for Uncertainty Evaluation

Radiochemical laboratories have long recognized the need to provide uncertainties with their results. Almost from the beginning, laboratories have provided the counting uncertainty for each result, because it is usually

[1] Planners and decisionmakers must also consider the variability of the analyte in sampled populations, as discussed in Appendix C; however, the focus of this chapter is on the uncertainty of measuring the analyte in each laboratory sample.

easy to evaluate (see Sections 19.3.5 and 19.5.2). However, the counting uncertainty is only one component of the total measurement uncertainty. Over the years it has been recommended repeatedly that laboratories perform good evaluations of the total uncertainty of each measurement. In 1980 the Environmental Protection Agency published a report entitled "Upgrading Environmental Radiation Data," which was produced by an ad hoc committee of the Health Physics Society. Two of the recommendations of this report were stated as follows (EPA 1980).

> Every reported measurement result (x) should include an estimate of its overall uncertainty (u_x) which is based on as nearly a complete an assessment as possible.
>
> The uncertainty assessment should include every conceivable or likely source of inaccuracy in the result.

More recently ANSI N42.23, *American National Standard Measurement and Associated Instrument Quality Assurance for Radioassay Laboratories*, recommended that service laboratories report both the counting uncertainty and the total propagated uncertainty. ISO/IEC 17025, *General Requirements for the Competence of Testing and Calibration Laboratories*, which was released as a standard in 1999, requires calibration and testing laboratories to "have and apply" procedures for estimating measurement uncertainties (ISO/IEC, 1999). The National Environmental Laboratory Accreditation Conference (NELAC) has also published a standard on laboratory quality systems, which requires a radiochemical testing laboratory to report with each result its associated measurement uncertainty (NELAC, 2002, ch. 5).

Note that the concept of *traceability* (see Chapter 18) is defined in terms of uncertainty. Traceability is defined as the "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" (ISO, 1993a). Thus, a laboratory cannot realistically claim that its measurement results are "traceable" to a standard unless there exists a chain of comparisons, each with an associated uncertainty, connecting its results to that standard.

This chapter considers only measurement uncertainty. The claim is often made that field sampling uncertainties are so large that they dwarf laboratory measurement uncertainties. Although the claim may be true in some cases, MARLAP rejects this argument as an excuse for failing to perform a full evaluation of the measurement uncertainty. A realistic estimate of the measurement uncertainty is one of the most useful quality indicators for a result.

Although the need for good uncertainty evaluation has long been recognized, not all laboratories have been able to implement the recommendations fully. A certain level of mathematical sophistication is required. Implementation requires, at a minimum, a mastery of basic algebra, some knowledge of differential calculus and a grasp of many concepts of probability and statistics; but even more fundamentally it requires an understanding of the various aspects of the measurement

process in the laboratory, including chemical and physical principles as well as practical considerations. Implementation at a laboratory is certainly easier if there are those who understand both the measurement process and the mathematical methods, but in some cases it may be necessary to use a team approach that brings together all the required expertise.

Today there is software that performs the mathematical operations for uncertainty evaluation and propagation, and some of the difficulties of implementation may disappear as such software becomes more widely available. Nevertheless analysts and technicians will still need to understand the concepts of measurement uncertainty and how they apply to particular measurement processes in the laboratory.

19.3 Evaluating and Expressing Measurement Uncertainty

The methods, terms, and symbols recommended by MARLAP for evaluating and expressing measurement uncertainty are described in the *Guide to the Expression of Uncertainty in Measurement*, hereafter abbreviated as *GUM*, which was published by the International Organization for Standardization (ISO) in 1993 and corrected and reprinted in 1995 (ISO, 1995). The methods presented in the *GUM* are summarized in this chapter and adapted for application to radiochemistry.

The terminology and notation used by the *GUM* and this chapter may be unfamiliar or confusing to readers who are familiar with statistics but not metrology. Metrology (the science of measurement) uses the language and methods of probability and statistics, but adds to them its own terms, symbols, and approximation methods.

19.3.1 Measurement, Error, and Uncertainty

The result of a measurement is generally used to estimate some particular quantity called the *measurand*. For example, the measurand for a radioactivity measurement might be the specific activity of ^{238}Pu in a laboratory sample. The difference between the measured result and the actual value of the measurand is the *error* of the measurement. Both the measured result and the error may vary with each repetition of the measurement, while the value of the measurand (the true value) remains fixed.

Measurement error may be caused by *random effects* and *systematic effects* in the measurement process. Random effects cause the measured result to vary randomly when the measurement is repeated. Systematic effects cause the result to tend to differ from the value of the measurand by a constant absolute or relative amount, or to vary in a nonrandom manner. Generally, both random and systematic effects are present in a measurement process.

A measurement error produced by a random effect is a *random error*, and an error produced by a systematic effect is a *systematic error*. A systematic error is often called a "bias" (see also Attachment 19A).[2] The distinction between random and systematic errors depends on the specification of the measurement process, since a random error in one measurement process may appear systematic in another. For example, a random error in the measurement of the specific activity of a radioactive standard solution may be systematic from the point of view of a laboratory that purchases the solution and uses it to calibrate instruments for other measurements.

Measurement errors may also be *spurious errors*, such as those caused by human *blunders* and instrument malfunctions. Blunders and other spurious errors are not taken into account in the statistical evaluation of measurement uncertainty. They should be avoided, if possible, by the use of good laboratory practices, or at least detected and corrected by appropriate quality assurance and quality control.

The error of a measurement is unknowable, because one cannot know the error without knowing the true value of the quantity being measured (the measurand). For this reason, the error is primarily a theoretical concept. However, the *uncertainty* of a measurement is a concept with practical uses. According to the *GUM*, the term "uncertainty of measurement" denotes a "parameter, associated with the result of a measurement, that characterizes the dispersion of the values that could reasonably be attributed to the measurand." The uncertainty of a measured value thus gives a bound for the likely size of the measurement error. In practice, there is seldom a need to refer to the error of a measurement, but an uncertainty should be stated for every measured result.

19.3.2 The Measurement Process

The International Union of Pure and Applied Chemistry (IUPAC) defines a (chemical) measurement process as an "analytical method of defined structure that has been brought into a state of statistical control, such that its imprecision and bias are fixed, given the measurement conditions" (IUPAC, 1995). The requirement of statistical control is an important aspect of the definition, since it is crucial to the determination of realistic uncertainty estimates. Statistical control implies that the measurement process is stable with a predictable distribution of results, and is a prerequisite for uncertainty evaluation and for the determination of process performance characteristics, such as the detection and quantification capabilities (see Chapter 20).

The laboratory ensures that the measurement process remains in a state of statistical control by following appropriate quality control (QC) procedures, as described in Chapter 18. Procedures

[2] In some performance-testing programs, the term "bias" is used to mean the difference between a laboratory's measured result and the target value. For example, one of the two definitions of bias stated in ANSI N13.30, "Performance Criteria for Radiobioassay," is the "deviation of a single measured value of a random variable from a corresponding expected value." MARLAP notes that such a deviation, even if it is large, may not give a reliable indication of bias in the statistical or metrological sense.

for statistical QC can be designed not only to ensure process stability but also to obtain data for use in the evaluation of measurement uncertainties.

The first step in defining a measurement process is to define the measurand clearly. The specification of the measurand is always ambiguous to some extent, but it should be as clear as necessary for the intended purpose of the data.[3] For example, when measuring the activity of a radionuclide in a laboratory sample, it is generally necessary to specify the activity as of a certain date and time and whether the entire sample or only a certain fraction is of interest. For very accurate work, it may be necessary to specify other conditions, such as temperature (e.g., activity concentration at 20 °C).

Often the measurand is not measured directly but instead an estimate is calculated from the measured values of other *input quantities*, which have a known mathematical relationship to the measurand. For example, input quantities in a measurement of radioactivity may include the gross count, blank or background count, counting efficiency and test portion size. So, another important aspect of the measurement process is the mathematical model for the relationship between the *output quantity*, Y, and measurable input quantities, $X_1, X_2, \ldots, X_N$, on which its value depends. The relationship will be expressed here abstractly as $Y = f(X_1, X_2, \ldots, X_N)$, but in practice the actual relationship may be expressed using a set of equations. What is important about a mathematical model is that it describes exactly how the value of the output quantity depends on the values of the input quantities.

The mathematical model for a radioactivity measurement often has the general form

$$Y = \frac{(\text{Gross Instrument Signal}) - (\text{Blank Signal} + \text{Estimated Interferences})}{\text{Sensitivity}}$$

Each of the quantities shown here may actually be a more complicated expression. For example, the sensitivity (the ratio of the net signal to the measurand) may be the product of factors such as the mass of the test portion, the chemical yield (recovery) and the instrument counting efficiency.

When the measurement is performed, a value x_i is estimated for each input quantity, X_i, and an estimated value, y, of the measurand is calculated using the relationship $y = f(x_1, x_2, \ldots, x_N)$.[4] Since there is an uncertainty in each *input estimate*, x_i, there is also an uncertainty in the *output esti-*

[3] Because of the unavoidable ambiguity in the specification of the measurand, one should, to be precise, speak of "a value" of the measurand and not "the value."

[4] In accordance with the *GUM*, an uppercase letter is used here to denote both the input or output quantity and the random variable associated with its measurement, while a lowercase letter is used for the estimated value of the quantity. For simplicity, in most of the later examples this convention will be abandoned. Only one symbol will be used for the quantity, the random variable, and the estimated value of the quantity.

mate, y. In order to obtain a complete estimate of the uncertainty of y, all input quantities that could have a potentially significant effect on y should be included in the model.

19.3.3 Analysis of Measurement Uncertainty

Determining the uncertainty of the output estimate y requires that the uncertainties of all the input estimates x_i be determined and expressed in comparable forms. The uncertainty of x_i is expressed in the form of an estimated standard deviation, called the *standard uncertainty* and denoted by $u(x_i)$, or in the form of an estimated variance, denoted by $u^2(x_i)$, which is the square of the standard uncertainty. A standard uncertainty is sometimes informally called a "one-sigma" uncertainty. The ratio $u(x_i) / |x_i|$ is called the *relative standard uncertainty* of x_i, which may be denoted by $u_r(x_i)$. If the input estimates are potentially correlated, covariance estimates $u(x_i,x_j)$ must also be determined. The covariance $u(x_i,x_j)$ is often recorded and presented in the form of an estimated correlation coefficient, $r(x_i,x_j)$, which is defined as the quotient $u(x_i,x_j) / u(x_i)u(x_j)$. The standard uncertainties and estimated covariances are combined to obtain the *combined standard uncertainty* of y, denoted by $u_c(y)$. (The term "total propagated uncertainty," or TPU, has been used for the same concept; however, MARLAP recommends the *GUM*'s terminology.) The square of the combined standard uncertainty, denoted by $u_c^2(y)$, is called the *combined variance*.

The mathematical operation of combining the standard uncertainties of the input estimates, $x_1,x_2,\ldots,x_N$, to obtain the combined standard uncertainty of the output estimate, y, is called "uncertainty propagation." Mathematical methods for propagating uncertainty and for evaluating the standard uncertainties of the input estimates are described in Section 19.4.

When one repeats a measurement many times, the observed standard deviation is generated primarily by random measurement errors and not by those systematic errors that remain fixed from one measurement to the next. Although the combined standard uncertainty of a result is expressed in the form of an estimated standard deviation, it is intended to account for both random and systematic errors, and for this reason it should tend to be somewhat larger than the standard deviation that is observed in repeated measurements. So, if the measurement is repeated many times and the observed standard deviation is substantially larger than the combined standard uncertainties of the results, one may conclude that the uncertainties are being underestimated.

Methods for evaluating the standard uncertainties $u(x_i)$ are classified as either Type A or Type B. A *Type A* evaluation is a statistical evaluation based on repeated observations. One typical example of a Type A evaluation involves making a series of independent measurements of a quantity, X_i, and calculating the arithmetic mean and the experimental standard deviation of the mean. The arithmetic mean is used as the input estimate, x_i, and the experimental standard deviation of the mean is used as the standard uncertainty, $u(x_i)$. There are other Type A methods, but all are based on repeated measurements. Any evaluation of standard uncertainty that is not a Type A evaluation is a *Type B* evaluation.

Sometimes a Type B evaluation of uncertainty involves making a best guess based on all available information and professional judgment. Laboratory workers may be reluctant to make this kind of evaluation, but it is better to make an informed guess about an uncertainty component than to ignore it completely.

A standard uncertainty $u(x_i)$ may be called a "Type A" or "Type B" standard uncertainty, depending on its method of evaluation, but no distinction is made between the two types for the purposes of uncertainty propagation.

19.3.4 Corrections for Systematic Effects

When a systematic effect in the measurement process has been identified and quantified, a quantity should be included in the mathematical measurement model to correct for it. The quantity, called a *correction* (additive) or *correction factor* (multiplicative), will have an uncertainty which should be evaluated and propagated.

Whenever a previously unrecognized systematic effect is detected, the effect should be investigated and either eliminated procedurally or corrected mathematically.

19.3.5 Counting Uncertainty

The *counting uncertainty* of a radiation measurement (historically called "counting error") is the component of uncertainty caused by the random nature of radioactive decay and radiation counting. Radioactive decay is inherently random in the sense that two atoms of a radionuclide will generally decay at different times, even if they are identical in every discernible way. Radiation counting is also inherently random unless the efficiency of the counting instrument is 100 %.

In many cases the counting uncertainty in a single gross radiation counting measurement can be estimated by the square root of the observed counts. The Poisson model of radiation counting, which is the mathematical basis for this rule, is discussed in Section 19.5. Note that the use of this approximation is a Type B evaluation of uncertainty.

Historically many radiochemistry laboratories reported only the counting uncertainties of their measured results. MARLAP recommends that a laboratory consider all possible sources of measurement uncertainty and evaluate and propagate the uncertainties from all sources believed to be potentially significant in the final result.

19.3.6 Expanded Uncertainty

When a laboratory reports the result of a measurement, it may report the combined standard uncertainty, $u_c(y)$, or it may multiply $u_c(y)$ by a factor k, called a *coverage factor*, to produce an *expanded uncertainty*, denoted by U, such that the interval from $y - U$ to $y + U$ has a specified

high probability p of containing the value of the measurand. The specified probability, p, is called the *level of confidence* or the *coverage probability* and is generally only an approximation of the true probability of coverage.

When the distribution of the measured result is approximately normal, the coverage factor is often chosen to be $k = 2$ for a coverage probability of approximately 95 %. An expanded uncertainty calculated with $k = 2$ or 3 is sometimes informally called a "two-sigma" or "three-sigma" uncertainty. In general, if the desired coverage probability is γ and the combined standard uncertainty is believed to be an accurate estimate of the standard deviation of the measurement process, the coverage factor for a normally distributed result is $k = z_{(1+\gamma)/2}$, which can be found in a table of quantiles of the standard normal distribution (see Table G.1 in Appendix G).

The *GUM* recommends the use of coverage factors in the range 2–3 when the combined standard uncertainty represents a good estimate of the true standard deviation. Attachment 19D describes a more general procedure for calculating the coverage factor, k_p, that gives a desired coverage probability p when there is substantial uncertainty in the value of $u_c(y)$.

The *GUM* does not assign a name to the interval $y \pm U$, but it clearly states that the interval should not be called a "confidence interval," because this term has a precise statistical definition and the interval described by the expanded uncertainty usually does not meet the requirements. The interval $y \pm U$ is sometimes called an "uncertainty interval."[5]

19.3.7 Significant Figures

The number of significant figures that should be reported for the result of a measurement depends on the uncertainty of the result. A common convention is to round the uncertainty (standard uncertainty or expanded uncertainty) to either one or two significant figures and to report both the measured value and the uncertainty to the resulting number of decimal places (ISO, 1995; Bevington, 1992; EPA, 1980; ANSI N42.23). MARLAP recommends this convention and suggests that uncertainties be rounded to two figures. The following examples demonstrate the application of the rule.

[5] When the distribution of the result is highly asymmetric, so that the result is more likely to fall on one side of the value of the measurand than the other, the use of a single expanded uncertainty, U, to construct a symmetric uncertainty interval about the result may be misleading, especially if one wishes to state an approximate coverage probability for the interval. However, methods for constructing an asymmetric uncertainty interval with a stated coverage probability are beyond the scope of this chapter and require more information than that provided by the input estimates, their standard uncertainties, and estimated covariances (e.g., Monte Carlo simulation). Note that the value of the combined standard uncertainty is unaffected by the symmetry or asymmetry of the distribution.

EXAMPLES

MEASURED VALUE (y)	EXPANDED UNCERTAINTY $U = k u_c(y)$	REPORTED RESULT
0.8961	0.0234	0.896 ± 0.023
0.8961	0.2342	0.90 ± 0.23
0.8961	2.3419	0.9 ± 2.3
0.8961	23.4194	1 ± 23
0.8961	234.1944	0 ± 230

Only final results should be rounded in this manner. Intermediate results in a series of calculation steps should be carried through all steps with additional figures to prevent unnecessary roundoff errors. Additional figures are also recommended when the data are stored electronically. Rounding should be performed only when the result is reported. (See Section 19.5.11 for a discussion of the measurement uncertainty associated with rounding.)

19.3.8 Reporting the Measurement Uncertainty

When a measured value y is reported, its uncertainty should always be stated. The laboratory may report either the combined standard uncertainty $u_c(y)$ or the expanded uncertainty U.

The measured value, y, and its expanded uncertainty, U, may be reported in the format $y \pm U$ or y +– U.

The plus-minus format may be used to report an expanded uncertainty, but it generally should be avoided when reporting a standard uncertainty, because readers are likely to interpret it as a confidence interval with a high coverage probability. A commonly used shorthand format for reporting a result with its standard uncertainty places the one or two digits of the standard uncertainty in parentheses immediately after the corresponding final digits of the rounded result. For example, if the rounded result of the measurement is 1.92 and the standard uncertainty is 0.14, the result and uncertainty may be shown together as 1.92(14). Another acceptable reporting format places the entire standard uncertainty in parentheses. The result in the preceding example would appear in this format as 1.92(0.14). The laboratory may also report the standard uncertainty explicitly.

Since laboratories may calculate uncertainties using different methods and report them using different coverage factors, it is a bad practice to report an uncertainty without explaining what it represents. Any analytical report, even one consisting of only a table of results, should state

whether the uncertainty is the combined standard uncertainty or an expanded uncertainty, and in the latter case it should also state the coverage factor used and, if possible, the approximate coverage probability. A complete report should also describe the methods used to calculate the uncertainties. If the laboratory uses a shorthand format for the uncertainty, the report should include an explanation of the format.

The uncertainties for environmental radioactivity measurements should be reported in the same units as the results. Relative uncertainties (i.e., uncertainties expressed as percentages) may also be reported, but the reporting of relative uncertainties alone is not recommended when the measured value may be zero, because the relative uncertainty in this case is undefined. A particularly bad practice, sometimes implemented in software, is to compute the relative uncertainty first and multiply it by the measured value to obtain the absolute uncertainty. When the measured value is zero, the uncertainty is reported incorrectly as zero. Reporting of relative uncertainties without absolute uncertainties for measurements of spiked samples or standards generally presents no problems, because the probability of a negative or zero result is negligible.

It is possible to calculate radioanalytical results that are less than zero, although negative radioactivity is physically impossible. Laboratories sometimes choose not to report negative results or results that are near zero. Such censoring of results is *not* recommended. *All results, whether positive, negative, or zero, should be reported as obtained, together with their uncertainties.*

The preceding statement must be qualified, because a measured value y may be so far below zero that it indicates a possible blunder, procedural failure, or other quality control problem. Usually, if $y + 3u_c(y) < 0$, the result should be considered invalid, although the accuracy of the uncertainty estimate $u_c(y)$ must be considered, especially in cases where only few counts are observed during the measurement and counting uncertainty is the dominant component of $u_c(y)$. (See Chapter 18, *Laboratory Quality Control*, and Attachment 19D of this chapter.)

19.3.9 Recommendations

MARLAP makes the following recommendations to radioanalytical laboratories.

- All radioanalytical laboratories should adopt the terminology and methods of the *Guide to the Expression of Uncertainty in Measurement* (ISO, 1995) for evaluating and reporting measurement uncertainty.

- The laboratory should follow QC procedures that ensure the measurement process remains in a state of statistical control, which is a prerequisite for uncertainty evaluation.

- Uncertainty estimates should account for both random and systematic effects in the measurement process, but they should not account for possible blunders or other spurious errors. Spurious errors indicate a loss of statistical control of the process.

- The laboratory should report each measured value with either its combined standard uncertainty or its expanded uncertainty.

- The reported measurement uncertainties should be clearly explained. In particular, when an expanded uncertainty is reported, the coverage factor should be stated, and, if possible, the approximate coverage probability should also be given.

- A laboratory should consider all possible sources of measurement uncertainty and evaluate and propagate the uncertainties from all sources believed to be potentially significant in the final result.

- Each uncertainty should be rounded to either one or two significant figures, and the measured value should be rounded to the same number of decimal places as its uncertainty. (MARLAP prefers the use of two figures in the uncertainty.) Only final results should be rounded in this manner.

- The laboratory should report all results, whether positive, negative, or zero, as obtained, together with their uncertainties.

MARLAP makes no recommendations regarding the presentation of radioanalytical data by the laboratory's clients or other end users of the data.

19.4 Procedures for Evaluating Uncertainty

The usual steps for evaluating and reporting the uncertainty of a measurement may be summarized as follows (adapted from Chapter 8 of the *GUM*):

1. Identify the measurand, Y, and all the input quantities, X_i, for the mathematical model. Include all quantities whose variability or uncertainty could have a potentially significant effect on the result. Express the mathematical relationship, $Y = f(X_1, X_2, \ldots, X_N)$, between the measurand and the input quantities.

2. Determine an estimate, x_i, of the value of each input quantity, X_i (an "input estimate," as defined in Section 19.3.2).

3. Evaluate the standard uncertainty, $u(x_i)$, for each input estimate, x_i, using either a Type A or Type B method of evaluation (see Section 19.3.3).

4. Evaluate the covariances, $u(x_i, x_j)$, for all pairs of input estimates with potentially significant correlations.

5. Calculate the estimate, y, of the measurand from the relationship $y = f(x_1, x_2, \ldots, x_N)$, where f is the function determined in Step 1.

6. Determine the combined standard uncertainty, $u_c(y)$, of the estimate, y (see Section 19.3.3).

7. Optionally multiply $u_c(y)$ by a coverage factor k to obtain the expanded uncertainty U such that the interval $[y - U, y + U]$ can be expected to contain the value of the measurand with a specified probability (see Section 19.3.6 and Attachment 19D).

8. Report the result as $y \pm U$ with the unit of measurement, and, at a minimum, state the coverage factor used to compute U and the estimated coverage probability. Alternatively, report the result, y, and its combined standard uncertainty, $u_c(y)$, with the unit of measurement.

19.4.1 Identifying Sources of Uncertainty

The procedure for assessing the uncertainty of a measurement begins with listing all conceivable sources of uncertainty in the measurement process. Even if a mathematical model has been identified, further thought may lead to the inclusion of more quantities in the model. Some sources of uncertainty will be more significant than others, but all should be listed.

After all conceivable sources of uncertainty are listed, they should be categorized as either potentially significant or negligible. Each uncertainty that is potentially significant should be evaluated quantitatively. The following sources of uncertainty may not always be significant but should at least be considered:

- radiation counting
- instrument calibration (e.g., counting efficiency)
- tracers, carriers, or other methods of yield measurement
- variable instrument backgrounds
- variable counting efficiency (e.g., due to the instrument or to source geometry and placement)
- contamination of reagents and tracers
- interferences, such as crosstalk and spillover
- baseline determination (gamma-ray spectrometry)
- laboratory subsampling

Other sources of uncertainty include:

- volume and mass measurements
- determination of counting time and correction for dead time

- time measurements used in decay and ingrowth calculations
- approximation errors in simplified mathematical models
- published values for half-lives and radiation emission probabilities

NOTE: MARLAP does not recommend that laboratories expend tremendous effort on the evaluation of small components of uncertainty when much larger components are known to dominate the combined standard uncertainty of the result. However, this chapter does provide guidance in several places on the evaluation of very small uncertainties. Such examples may be instructive even if the uncertainties are negligible, because they illustrate either important concepts or possible methods of uncertainty evaluation. Furthermore, an uncertainty component that is negligible in one context (e.g., pipetting uncertainty in the context of measuring the activity of a radionuclide in a soil sample) may be considered significant in another (e.g., quality control of measuring instruments). It is also true that a very large number of small uncertainties may be significant when combined.

19.4.2 Evaluation of Standard Uncertainties

Calculating the combined standard uncertainty of an output estimate $y = f(x_1, x_2, \ldots, x_N)$ requires the evaluation of the standard uncertainty of each input estimate, x_i. As stated earlier, methods for evaluating standard uncertainties are classified as either "Type A" or "Type B." A Type A evaluation of an uncertainty uses a series of measurements to estimate the standard deviation empirically. Any other method of evaluating an uncertainty is a Type B method.

In general, the standard uncertainty of an input estimate, x_i, is an estimated standard deviation for the estimator whose value is used for x_i. The appropriate methods for estimating this standard deviation depend on how the value of the input estimate is obtained.

19.4.2.1 Type A Evaluations

Suppose X_i is an input quantity in the mathematical model. If a series of n independent observations of X_i are made under the same measurement conditions, yielding the results $X_{i,1}, X_{i,2}, \ldots, X_{i,n}$, the appropriate value for the input estimate x_i is the *arithmetic mean*, or *average*, $\overline{X}_i$, defined as

$$\overline{X}_i = \frac{1}{n} \sum_{k=1}^{n} X_{i,k} \tag{19.1}$$

The *experimental variance* of the observed values is defined as

$$s^2(X_{i,k}) = \frac{1}{n-1} \sum_{k=1}^{n} (X_{i,k} - \overline{X}_i)^2 \tag{19.2}$$

and the *experimental standard deviation*, $s(X_{i,k})$, is the square root of $s^2(X_{i,k})$. The *experimental standard deviation of the mean*, $s(\overline{X}_i)$, is obtained by dividing $s(X_{i,k})$ by $\sqrt{n}$.[6]

$$s(\overline{X}_i) = \frac{s(X_{i,k})}{\sqrt{n}} \tag{19.3}$$

The experimental standard deviation of the mean is also commonly called the "standard error of the mean."

The Type A standard uncertainty of the input estimate $x_i = \overline{X}_i$ is defined to be the experimental standard deviation of the mean. Combining the preceding formulas gives the following equation for the standard uncertainty of x_i:

$$u(x_i) = \sqrt{\frac{1}{n(n-1)} \sum_{k=1}^{n} (X_{i,k} - \overline{X}_i)^2} \tag{19.4}$$

When the input estimate x_i and standard uncertainty $u(x_i)$ are evaluated as described above, the number of *degrees of freedom* for the evaluation is equal to $n - 1$, or one less than the number of independent measurements of the quantity X_i. In general, the number of degrees of freedom for a statistical determination of a set of quantities equals the number of independent observations minus the number of quantities estimated. The number of degrees of freedom for each evaluation of standard uncertainty is needed to implement the procedure for calculating coverage factors described in Attachment 19D.

EXAMPLE 19.1 Ten independent measurements of a quantity X_i are made, yielding the values

12.132	12.139	12.128	12.133	12.132
12.135	12.130	12.129	12.134	12.136

The estimated value x_i is the arithmetic mean of the values $X_{i,k}$.

$$x_i = \overline{X}_i = \frac{1}{n} \sum_{k=1}^{n} X_{i,k} = \frac{121.328}{10} = 12.1328$$

[6] The experimental standard deviation of the mean, $s(\overline{X}_i)$, may be used as the standard uncertainty of the average, $\overline{X}_i$, even if the individual observations $X_{i,k}$ are obtained under different conditions of measurement, so long as all pairs of distinct observations, $X_{i,k}$ and $X_{i,\ell}$, can be considered to be uncorrelated. However, in these circumstances, it is sometimes better to define the input estimate, x_i, to be a *weighted* average of the observations.

The standard uncertainty of x_i is

$$u(x_i) = s(\overline{X}_i) = \sqrt{\frac{1}{n\,(n-1)} \sum_{k=1}^{n} (X_{i,k} - \overline{X}_i)^2}$$

$$= \sqrt{\frac{1}{10\,(10-1)} \sum_{k=1}^{10} (X_{i,k} - 12.1328)^2}$$

$$= \sqrt{1.12889 \times 10^{-6}} \quad = 0.0011$$

USE OF HISTORICAL DATA

In some cases there may be accumulated data for a measurement system, such as a balance or pipet, which can be used in a Type A evaluation of uncertainty for future measurements, assuming the measurement process remains in control. In fact the use of recent historical data is advisable in such cases, because it enlarges the pool of data available for uncertainty evaluation and increases the number of degrees of freedom. This type of uncertainty evaluation can be linked closely to the measurement system's routine quality control.

One may pool recent historical data with current measurement data, or one may evaluate an uncertainty based on historical data alone. The appropriate expression for the standard uncertainty depends on how the data are used to calculate the input estimate, x_i, and on whether x_i is used to *estimate* the value of a parameter or to *predict* the value of a variable. An example of estimating the value of a parameter is measuring the mass of material in a container using an analytical balance. An example of predicting the value of a variable is calibrating a pipet, since the actual volumes dispensed by the pipet in subsequent measurements vary and are seldom measured directly.

Attachment 19E provides descriptions and examples of the use of historical data for Type A evaluations of uncertainty in mass and volume measurements.

EVALUATION OF COVARIANCE

If X_i and X_j are two input quantities and estimates of their values are correlated, a Type A evaluation of covariance may be performed by making n independent pairs of simultaneous observations of X_i and X_j and calculating the experimental covariance of the means. If the observed pairs are $(X_{i,1},X_{j,1})$, $(X_{i,2},X_{j,2})$, …, $(X_{i,n},X_{j,n})$, the *experimental covariance* of the values is

$$s(X_{i,k},X_{j,k}) = \frac{1}{n-1}\sum_{k=1}^{n}(X_{i,k}-\overline{X}_i)(X_{j,k}-\overline{X}_j) \tag{19.5}$$

and the *experimental covariance of the means* $\overline{X}_i$ and $\overline{X}_j$ is

$$s(\overline{X}_i,\overline{X}_j) = \frac{s(X_{i,k},X_{j,k})}{n} \tag{19.6}$$

So, the Type A covariance of the input estimates $x_i = \overline{X}_i$ and $x_j = \overline{X}_j$ is

$$u(x_i,x_j) = s(\overline{X}_i,\overline{X}_j) = \frac{1}{n(n-1)}\sum_{k=1}^{n}(X_{i,k}-\overline{X}_i)(X_{j,k}-\overline{X}_j) \tag{19.7}$$

An evaluation of variances and covariances of quantities determined by the method of least squares may also be a Type A evaluation.

19.4.2.2 Type B Evaluations

There are many ways to perform Type B evaluations of standard uncertainty. This section describes some common Type B evaluations but is not meant to be exhaustive.

POISSON COUNTING UNCERTAINTY

One example of a Type B method already given is the estimation of counting uncertainty using the square root of the observed counts. If the observed count is N, when the Poisson approximation is used, the standard uncertainty of N may be evaluated as $u(N) = \sqrt{N}$. When N may be very small or even zero, MARLAP recommends the use of the equation $u(N) = \sqrt{N+1}$ instead (see Attachment 19D).

EXAMPLE 19.2 A Poisson counting measurement is performed, during which $N = 121$ counts are observed. So, the standard uncertainty of N is $u(N) = \sqrt{121} = 11$.

RECTANGULAR DISTRIBUTION

Sometimes a Type B evaluation of an uncertainty $u(x)$ consists of estimating an upper bound a for the magnitude of the error of x based on professional judgment and the best available information. If nothing else is known about the distribution of the measured result, then after a is estimated, the standard uncertainty may be calculated using the equation

$$u(x) = \frac{a}{\sqrt{3}} \tag{19.8}$$

which is derived from a statistical model in which the error has a *rectangular*, or *uniform*, distribution bounded by $-a$ and $+a$ (see Section 19A.6 in Attachment 19A).

EXAMPLE 19.3 The maximum error of a measured value $x = 34.40$ is estimated to be $a = 0.05$, with all values between 34.35 and 34.45 considered equally likely. So, the standard uncertainty of x is $u(x) = 0.05 / \sqrt{3} = 0.029$.

EXAMPLE 19.4 A strontium carrier solution is prepared by dissolving strontium nitrate in acidified water. The purity, P, of the strontium nitrate is stated to be 99.9 %, or 0.999, but no tolerance or uncertainty is provided. By default, a rectangular distribution with half-width $1 - P$, or 0.001, is assumed. So, the standard uncertainty of P is evaluated as $u(P) = 0.001 / \sqrt{3} = 0.00058$.

TRAPEZOIDAL DISTRIBUTION

It may also happen that one can estimate an upper bound, a, for the magnitude of the error so that the input quantity is believed with near certainty to lie between $x - a$ and $x + a$, but one believes that values near x are more likely than those near the extremes, $x \pm a$. In this case, a symmetric *trapezoidal* distribution may be used to obtain the standard uncertainty of x. The trapezoidal distribution is named for the fact that the graph of its pdf has the shape of a trapezoid (see Section 19A.7 in Attachment 19A). To use the trapezoidal model, one determines the value a, which represents the maximum possible error of the input estimate, and another value, β, which describes the fraction of possible values about the input estimate that are considered most likely ($0 < \beta < 1$). Then the standard uncertainty of x is given by the following expression.

$$u(x) = a\sqrt{\frac{1 + \beta^2}{6}} \tag{19.9}$$

As β approaches zero, the trapezoidal distribution becomes *triangular*, and the standard uncertainty of x approaches $a / \sqrt{6}$. As β approaches one, the trapezoidal distribution becomes rectangular, and the standard uncertainty of x approaches $a / \sqrt{3}$.

EXAMPLE 19.5 Extreme bounds for a quantity X are estimated to be 34.3 and 34.5, with values between 34.35 and 34.45 considered most likely. Using the trapezoidal model, one obtains the input estimate

$$x = \frac{34.3 + 34.5}{2}$$

the half-width

$$a = \frac{34.5 - 34.3}{2} = 0.1$$

and the fraction

$$\beta = \frac{34.45 - 34.35}{34.5 - 34.3} = \frac{0.1}{0.2} = 0.5$$

Then the standard uncertainty of x is calculated as follows.

$$u(x) = a\sqrt{\frac{1 + \beta^2}{6}} = 0.1\sqrt{\frac{1 + 0.5^2}{6}} = 0.046$$

EXAMPLE 19.6 The manufacturer of a 100-milliliter volumetric flask specifies that the capacity tolerance is 0.08 mL. The user of the flask assumes the tolerance represents the half-width of a triangular distribution and evaluates the standard uncertainty of the capacity to be $0.08 / \sqrt{6} = 0.033$ mL. (See Section 19.5.10 and Attachment 19E for more information about the uncertainty of a volume measurement.)

IMPORTED VALUES

When the estimate of an input quantity is taken from an external source, such as a book or a calibration certificate, which states the uncertainty as a multiple of the standard deviation s, the standard uncertainty is obtained by dividing the stated uncertainty by the stated multiplier of s.

EXAMPLE 19.7 The uncertainty for a measured activity concentration, c_A, is stated to be 0.015 Bq/L and the stated multiplier is 2. So, the standard uncertainty of c_A is $u(c_A) = 0.015 / 2 = 0.0075$ Bq/L.

If the estimate is provided by a source which gives a bound c for the error such that the interval from $x - c$ to $x + c$ contains the true value with 100γ % confidence ($0 < \gamma < 1$) but no other information about the distribution is given, the measured result may be assumed to have a normal distribution, and the standard uncertainty may therefore be evaluated as

$$u(x) = \frac{c}{z_{(1+\gamma)/2}} \tag{19.10}$$

The value of $z_{(1+\gamma)/2}$ may be found in a table of quantiles of the standard normal distribution (see Table G.1 in Appendix G).

EXAMPLE 19.8 The specific activity, x, of a commercial standard solution is stated to lie within the interval (4530 ± 64) Bq/g with 95 % confidence. The standard uncertainty may therefore be evaluated as $u(x) = 64 / z_{0.975} = 64 / 1.96 = 33$ Bq/g.

EVALUATION OF COVARIANCE

Evaluation of the covariance of two input estimates, x_i and x_j, whose uncertainties are evaluated by Type B methods may require expert judgment. Generally, in such cases it is simpler to estimate the correlation coefficient, $r(x_i,x_j)$, first and then multiply it by the standard uncertainties, $u(x_i)$ and $u(x_j)$ to obtain the covariance, $u(x_i,x_j)$. The correlation coefficient must be a number between −1 and +1. A correlation coefficient of zero indicates no correlation between the estimates, while a value of ±1 indicates the strongest possible correlation. Usually, if the two input estimates have a significant correlation, it is easy to guess the sign of the correlation coefficient, but estimating its magnitude may require knowledge and experience.

If the input estimates are imported values (e.g., from a published reference), the only practical method of evaluating their covariance is to use the correlation coefficient, if any, provided with the estimates. When no correlation coefficient is stated, the input estimates must be assumed to be uncorrelated.

In many cases when a correlation between two input estimates is suspected, the reason for the suspicion is that identifiable random or systematic effects in the measurement process are known to affect both estimates. It may be possible in such cases to include additional explicit variables in the mathematical model to account for those effects, eliminating the need for Type B covariance evaluations.

Sometimes two input estimates for one measurement model are explicitly calculated from other measured values. Section 19.4.4 shows how one may evaluate the covariance for two such calculated values.

19.4.3 Combined Standard Uncertainty

19.4.3.1 Uncertainty Propagation Formula

Consider the mathematical model $Y = f(X_1, X_2, \ldots, X_N)$. If $x_1, x_2, \ldots, x_N$ are measured values of the input quantities, X_i, and $y = f(x_1, x_2, \ldots, x_N)$ is the calculated value of the output quantity, Y, the combined standard uncertainty of y is obtained using the following formula.

$$u_c^2(y) = \sum_{i=1}^{N} \left(\frac{\partial f}{\partial x_i} \right)^2 u^2(x_i) + 2 \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \frac{\partial f}{\partial x_i} \frac{\partial f}{\partial x_j} u(x_i, x_j) \qquad (19.11)$$

Uncertainty Propagation Formula

Here $u^2(x_i)$ denotes the estimated variance of x_i, or the square of its standard uncertainty; $u(x_i, x_j)$ denotes the estimated covariance of x_i and x_j; $\partial f / \partial x_i$ (or $\partial y / \partial x_i$) denotes the partial derivative of f with respect to X_i evaluated at the measured values $x_1, x_2, \ldots, x_N$; and $u_c^2(y)$ denotes the combined variance of y, whose positive square root, $u_c(y)$, is the combined standard uncertainty of y. The partial derivatives, $\partial f / \partial x_i$, are called *sensitivity coefficients*.

The preceding formula, called the "law of propagation of uncertainty" in the *GUM*, will be called the "uncertainty propagation formula" or the "first-order uncertainty propagation formula" in this document. Equation 19.11 is commonly used to *define* the combined standard uncertainty, but note that the combined standard uncertainty is only an approximation of the true standard deviation of the output estimate, and sometimes other definitions provide better approximations (e.g., see Section 19.4.5.1).[7]

Table 19.1 shows several rules for partial differentiation, which tend to be useful when one calculates the sensitivity coefficients in the uncertainty propagation formula. Table 19.2 shows how to propagate uncertainties in some common cases. The expressions for the combined standard uncertainties shown in Table 19.2 may be derived from the uncertainty propagation formula using the differentiation rules listed in Table 19.1.

[7] The uncertainty propagation formula may be derived by approximating the function f by a first-order Taylor polynomial.

TABLE 19.1 — Differentiation rules

In the following equations the symbols F and G denote arbitrary expressions, which may contain the variables $x_1, x_2, \ldots, x_N$. The symbol c denotes either a constant expression or any other expression that does not contain the variable x_i.

$$\frac{\partial c}{\partial x_i} = 0 \qquad \frac{\partial (F \pm G)}{\partial x_i} = \frac{\partial F}{\partial x_i} \pm \frac{\partial G}{\partial x_i} \qquad \frac{\partial (F^c)}{\partial x_i} = cF^{c-1}\frac{\partial F}{\partial x_i}$$

$$\frac{\partial x_i}{\partial x_i} = 1 \qquad \frac{\partial (FG)}{\partial x_i} = \frac{\partial F}{\partial x_i}G + F\frac{\partial G}{\partial x_i} \qquad \frac{\partial (\mathrm{e}^F)}{\partial x_i} = \mathrm{e}^F\frac{\partial F}{\partial x_i}$$

$$\frac{\partial x_j}{\partial x_i} = 0, \text{ if } i \neq j \qquad \frac{\partial (F/G)}{\partial x_i} = \frac{(\partial F/\partial x_i)G - F(\partial G/\partial x_i)}{G^2} \qquad \frac{\partial (\ln F)}{\partial x_i} = \frac{\partial F/\partial x_i}{F}$$

$$\frac{\partial (cF)}{\partial x_i} = c\frac{\partial F}{\partial x_i} \qquad \frac{\partial (1/F)}{\partial x_i} = \frac{-\partial F/\partial x_i}{F^2} \qquad \frac{\partial (\log_{10} F)}{\partial x_i} = \frac{\partial F/\partial x_i}{(\ln 10)F}$$

TABLE 19.2 — Applications of the first-order uncertainty propagation formula

SUMS AND DIFFERENCES	If a and b are constants, then $$u_c^2(ax \pm by) = a^2u^2(x) + b^2u^2(y) \pm 2ab \cdot u(x,y)$$
PRODUCTS	If x and y are measured values, then $$u_c^2(xy) = u^2(x)y^2 + x^2u^2(y) + 2xy \cdot u(x,y)$$ When x and y are nonzero, the formula may be rewritten as $$u_c^2(xy) = x^2y^2\left(\frac{u^2(x)}{x^2} + \frac{u^2(y)}{y^2} + \frac{2u(x,y)}{xy}\right)$$
QUOTIENTS	If x and y are measured values, then $$u_c^2\left(\frac{x}{y}\right) = \frac{u^2(x)}{y^2} + \frac{x^2u^2(y)}{y^4} - \frac{2x \cdot u(x,y)}{y^3}$$ When x is nonzero, the variance formula may be rewritten as $$u_c^2\left(\frac{x}{y}\right) = \frac{x^2}{y^2}\left(\frac{u^2(x)}{x^2} + \frac{u^2(y)}{y^2} - \frac{2u(x,y)}{xy}\right)$$
EXPONENTIALS	If a is a constant, then $$u_c^2(\mathrm{e}^{ax}) = a^2\mathrm{e}^{2ax}u^2(x)$$ If n is a positive integral constant, then $$u_c^2(x^n) = n^2x^{2n-2}u^2(x)$$
LOGARITHMS	If a is a constant and ax is positive, then $$u_c^2(\ln ax) = \frac{u^2(x)}{x^2} \quad \text{and} \quad u_c^2(\log_{10} ax) = \frac{u^2(x)}{(\ln 10)^2x^2} \approx \frac{u^2(x)}{(5.302)x^2}$$

If the input estimates $x_1, x_2, \ldots, x_N$ are uncorrelated, the uncertainty propagation formula reduces to

$$u_c^2(y) = \sum_{i=1}^{N} \left(\frac{\partial f}{\partial x_i} \right)^2 u^2(x_i) \qquad (19.12)$$

Equation 19.12 is only valid when the input estimates are uncorrelated. Although this case occurs frequently in practice, there are notable exceptions. When input estimates are obtained using the same measuring devices or the same standard solutions, or when they are calculated from the same data, there is a potential for correlation. For example, instrument calibration parameters determined by least-squares analysis may be strongly correlated. Fortunately, the method of least squares provides covariance estimates with almost no additional effort (see Attachment 19C). In general, ignoring correlations between the input estimates may lead to overestimation or underestimation of the combined standard uncertainty.

EXAMPLE 19.9

Problem: A 6000-second gross-alpha measurement is performed on a test source prepared by evaporating water on a stainless steel planchet. The measurement produces 120 alpha counts. The preceding blank measurement on the instrument had a duration of 6000 s and produced 42 alpha counts. The estimated alpha-particle counting efficiency is 0.223 with a standard uncertainty of 0.015. The sample volume analyzed is 0.05000 L, with a standard uncertainty of 0.00019 L. The alpha-particle emission rate per unit volume is described by the mathematical model

$$c_\alpha = \frac{N_S / t_S - N_B / t_B}{\varepsilon V}$$

where

- c_α is the alpha-particle emission rate per unit volume;
- N_S is the source count ($N_S = 120$);
- N_B is the blank count ($N_B = 42$);
- t_S is the source count time ($t_S = 6000$ s);
- t_B is the blank count time ($t_B = 6000$ s);
- ε is the counting efficiency ($\varepsilon = 0.223$); and
- V is the volume analyzed ($V = 0.0500$ L).

What is the output estimate c_α and what is its combined standard uncertainty, $u_c(c_\alpha)$? (Use the Poisson approximation for the uncertainties of N_S and N_B.)

Solution: First compute the output estimate c_α (alpha particles per second per liter).

$$c_\alpha = \frac{N_S / t_S - N_B / t_B}{\varepsilon V} = \frac{120/6000 - 42/6000}{(0.223)(0.05000)} \approx 1.17 \text{ s}^{-1} \cdot \text{L}^{-1}$$

Then compute the combined standard uncertainty $u_c(c_\alpha)$. The only uncertainties included in the model will be those associated with the counts N_S and N_B, the efficiency ε, and the volume V. There is no reason to suspect correlations between the measured values; so, the uncertainty propagation formula becomes

$$u_c^2(c_\alpha) = \left(\frac{\partial c_\alpha}{\partial N_S}\right)^2 u^2(N_S) + \left(\frac{\partial c_\alpha}{\partial N_B}\right)^2 u^2(N_B) + \left(\frac{\partial c_\alpha}{\partial \varepsilon}\right)^2 u^2(\varepsilon) + \left(\frac{\partial c_\alpha}{\partial V}\right)^2 u^2(V)$$

The sensitivity coefficients are evaluated using the differentiation rules shown in Table 19.1:

$$\frac{\partial c_\alpha}{\partial N_S} = \frac{\partial (N_S / t_S - N_B / t_B) / \partial N_S}{\varepsilon V} = \frac{\partial (N_S / t_S) / \partial N_S - 0}{\varepsilon V} = \frac{\partial N_S / \partial N_S}{t_S \varepsilon V} = \frac{1}{t_S \varepsilon V} = 0.0149477 \text{ s}^{-1} \cdot \text{L}^{-1}$$

$$\frac{\partial c_\alpha}{\partial N_B} = \frac{\partial (N_S / t_S - N_B / t_B) / \partial N_B}{\varepsilon V} = \frac{0 - \partial (N_B / t_B) / \partial N_B}{\varepsilon V} = \frac{-\partial N_B / \partial N_B}{t_B \varepsilon V} = \frac{-1}{t_B \varepsilon V} = -0.0149477 \text{ s}^{-1} \cdot \text{L}^{-1}$$

$$\frac{\partial c_\alpha}{\partial \varepsilon} = -\frac{N_S / t_S - N_B / t_B}{\varepsilon^2 V} \frac{\partial \varepsilon}{\partial \varepsilon} = -\frac{N_S / t_S - N_B / t_B}{\varepsilon^2 V} = -5.22834 \text{ s}^{-1} \cdot \text{L}^{-1}$$

$$\frac{\partial c_\alpha}{\partial V} = -\frac{N_S / t_S - N_B / t_B}{\varepsilon V^2} \frac{\partial V}{\partial V} = -\frac{N_S / t_S - N_B / t_B}{\varepsilon V^2} = -23.3184 \text{ s}^{-1} \cdot \text{L}^{-2}$$

The Poisson approximation is used for the standard uncertainties of the counts N_S and N_B. So,

$$u^2(N_S) = N_S = 120 \quad \text{and} \quad u^2(N_B) = N_B = 42$$

Recall from the statement of the problem that $u(\varepsilon) = 0.015$ and $u(V) = 0.00019$. When the values of all these expressions are substituted into the uncertainty propagation formula, the combined variance is

$$\begin{aligned} u_c^2(c_\alpha) &= (0.0149477)^2(120) + (-0.0149477)^2(42) + (-5.22834)^2(0.015)^2 \\ &\quad + (-23.3184)^2(0.00019)^2 \\ &= 0.0424 \text{ s}^{-2} \cdot \text{L}^{-2} \end{aligned}$$

So, the combined standard uncertainty is $u_c(c_\alpha) = \sqrt{0.0424} \approx 0.21 \text{ s}^{-1} \cdot \text{L}^{-1}$.

19.4.3.2 Components of Uncertainty

The product of $|\partial f / \partial x_i|$ and the standard uncertainty $u(x_i)$ is called the *component* of the combined standard uncertainty *generated by* the standard uncertainty of x_i, and may be denoted by $u_i(y)$. When all the input estimates are uncorrelated, the combined standard uncertainty may be written in terms of its components as follows.

$$u_c^2(y) = \sum_{i=1}^{N} u_i^2(y) \tag{19.13}$$

Since $u_c^2(y)$ is the sum of the squares of the components $u_i(y)$, the combined standard uncertainty tends to be determined primarily by its largest components. When the input estimates are correlated, Equation 19.13 is replaced by

$$u_c^2(y) = \sum_{i=1}^{N} u_i^2(y) + 2 \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} r(x_i, x_j) u_i(y) u_j(y) \tag{19.14}$$

Recall that $r(x_i,x_j)$ denotes the estimated correlation coefficient of x_i and x_j.

Figure 19.1 relates Equation 19.13 to the Pythagorean theorem about right triangles to illustrate graphically how uncertainty components are added to produce the combined standard uncertainty in the case of a model, $y = f(x_1,x_2)$, with two uncorrelated input estimates, x_1 and x_2.

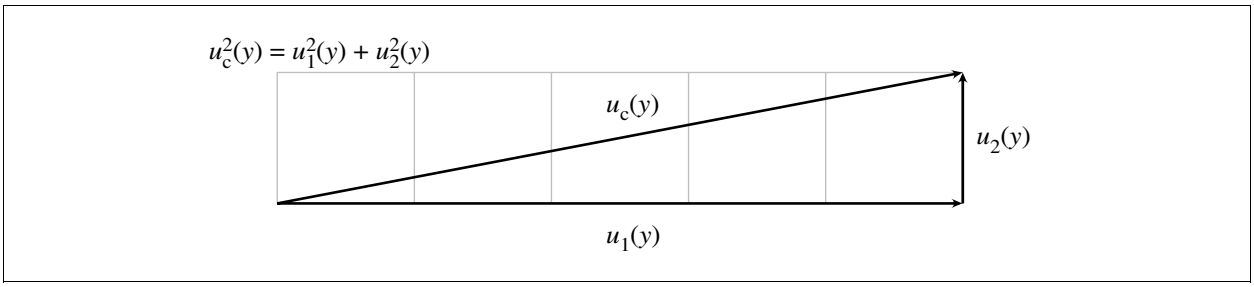

FIGURE 19.1 — Addition of uncertainty components

In the figure, the first component, $u_1(y)$, is five times larger than the second component, $u_2(y)$, and as a result the combined standard uncertainty, $u_c(y)$, is dominated by $u_1(y)$. Ignoring $u_2(y)$ in this case would decrease the combined standard uncertainty by only about 2 % of its value.

When the model involves more than two input quantities, the addition process shown in the figure may be iterated.[8]

19.4.3.3 Special Forms of the Uncertainty Propagation Formula

It is helpful to remember certain special forms of the uncertainty propagation formula. For example, if the values $x_1, x_2, \ldots, x_n$ and $z_1, z_2, \ldots, z_m$ are uncorrelated and nonzero, the combined standard uncertainty of $y = \frac{x_1 x_2 \cdots x_n}{z_1 z_2 \cdots z_m}$ may be calculated from the formula

$$u_c^2(y) = y^2 \left(\frac{u^2(x_1)}{x_1^2} + \frac{u^2(x_2)}{x_2^2} + \cdots + \frac{u^2(x_n)}{x_n^2} + \frac{u^2(z_1)}{z_1^2} + \frac{u^2(z_2)}{z_2^2} + \cdots + \frac{u^2(z_m)}{z_m^2} \right) \qquad (19.15)$$

As another example, suppose $y = \frac{f(x_1, x_2, \ldots, x_n)}{z_1 z_2 \cdots z_m}$, where f is some specified function of $x_1, x_2, \ldots, x_n$, all the z_i are nonzero, and all the input estimates are uncorrelated. Then

$$u_c^2(y) = \frac{u_c^2\left(f(x_1 x_2 \cdots x_n)\right)}{z_1^2 z_2^2 \cdots z_m^2} + y^2 \left(\frac{u^2(z_1)}{z_1^2} + \frac{u^2(z_2)}{z_2^2} + \cdots + \frac{u^2(z_m)}{z_m^2} \right) \qquad (19.16)$$

[8] When the two input estimates are correlated, the vectors that represent $u_1(y)$ and $u_2(y)$ may still be added graphically, but they are no longer perpendicular. In this case the correlation coefficient, $r(x_i, x_j)$, equals the cosine of the angle between the two vectors. When there are more than two input quantities, the existence of correlations among the input estimates makes the graphical addition method impractical.

Equation 19.16 is particularly useful in radiochemistry, where $f(x_1,x_2,\ldots,x_n)$ might be a net count rate and $z_1 z_2 \cdots z_m$ might be the product of the test portion size, chemical yield, counting efficiency, decay factor, and other sensitivity factors.

EXAMPLE 19.10 Consider the preceding gross-alpha example. Equation 19.16 implies the following equation for the combined variance of c_α.

$$u_c^2(c_\alpha) = \frac{u_c^2(N_S / t_S - N_B / t_B)}{\varepsilon^2 V^2} + c_\alpha^2 \left(\frac{u^2(\varepsilon)}{\varepsilon^2} + \frac{u^2(V)}{V^2} \right)$$

$$= \frac{u^2(N_S) / t_S^2 + u^2(N_B) / t_B^2}{\varepsilon^2 V^2} + c_\alpha^2 \left(\frac{u^2(\varepsilon)}{\varepsilon^2} + \frac{u^2(V)}{V^2} \right)$$

Then, since $u^2(N_S) = N_S$ and $u^2(N_B) = N_B$,

$$u_c^2(c_\alpha) = \frac{N_S / t_S^2 + N_B / t_B^2}{\varepsilon^2 V^2} + c_\alpha^2 \left(\frac{u^2(\varepsilon)}{\varepsilon^2} + \frac{u^2(V)}{V^2} \right)$$

$$= \frac{120 / (6000\ \text{s})^2 + 42 / (6000\ \text{s})^2}{(0.223)^2 (0.0500\ \text{L})^2} + (1.17\ \text{s}^{-1} \cdot \text{L}^{-1})^2 \left(\frac{0.015^2}{0.223^2} + \frac{(0.00019\ \text{L})^2}{(0.0500\ \text{L})^2} \right)$$

$$= 0.0424\ \text{s}^{-2} \cdot \text{L}^{-2}$$

and $u_c(c_\alpha) = 0.21\ \text{s}^{-1} \cdot \text{L}^{-1}$.

19.4.4 The Estimated Covariance of Two Output Estimates

Measured values obtained from two measurement processes may be correlated if some of the same input estimates are used to calculate output estimates in both models. If the two measured values are to be used as input quantities in a third model, their covariance must be estimated.

Suppose the combined set of input quantities in two mathematical models consists of $X_1, X_2, \ldots, X_N$. Then the models can be expressed as $Y = f(X_1,X_2,\ldots,X_N)$ and $Z = g(X_1,X_2,\ldots,X_N)$, where each of the measurands may actually depend on only a subset of the combined list of input quantities. If the input estimates are $x_1, x_2, \ldots, x_N$ and the output estimates are $y = f(x_1,x_2,\ldots,x_N)$ and $z = g(x_1,x_2,\ldots,x_N)$, the covariance of y and z is estimated by

$$u(y,z) = \sum_{i=1}^{N} \sum_{j=1}^{N} \frac{\partial f}{\partial x_i} \frac{\partial g}{\partial x_j} u(x_i,x_j) \qquad (19.17)$$

Since $u(y,y) = u_c^2(y)$, the preceding equation may be considered a generalization of the first-order uncertainty propagation formula.

Even when all the input estimates, x_i and x_j, are uncorrelated, the output estimates, y and z, may be correlated, but in this case Equation 19.17 reduces to the following.

$$u(y,z) = \sum_{i=1}^{N} \frac{\partial f}{\partial x_i} \frac{\partial g}{\partial x_i} u^2(x_i) \tag{19.18}$$

EXAMPLE 19.11 A radiation counter is calibrated for a certain source geometry and the counting efficiency is determined to be 0.423 with a standard uncertainty of 0.012. A 6000-second blank measurement is performed and 108 counts are recorded. Next two 3000-second measurements of a radioactive source in the required geometry are performed. The first measurement produces 1210 counts and the second produces 1244 counts. The activity of the source is calculated twice, using the model

$$A = \frac{N_S / t_S - N_B / t_B}{\varepsilon}$$

where

A	is the source activity;
N_S	is the count observed when the source is measured (1210 and 1244);
t_S	is the source count time (3000 s, negligible uncertainty);
N_B	is the count observed when the blank is measured;
t_B	is the blank count time (6000 s, negligible uncertainty); and
ε	is the counting efficiency (0.423 ± 0.012).

Let A_1 and A_2 denote the two calculated activities. Assuming all the input estimates are uncorrelated, estimate the covariance $u(A_1, A_2)$.

The standard uncertainties of N_S and N_B in each measurement are evaluated using the Poisson approximation. So, $u^2(N_S) = N_S$ and $u^2(N_B) = N_B$. Then Equation 19.16 can be used to calculate the combined standard uncertainty of each result, as shown below.

$$u_c^2(A) = \frac{u^2(N_S) / t_S^2 + u^2(N_B) / t_B^2}{\varepsilon^2} + A^2 \frac{u^2(\varepsilon)}{\varepsilon^2}$$

$$= \frac{N_S / t_S^2 + N_B / t_B^2}{\varepsilon^2} + A^2 \frac{u^2(\varepsilon)}{\varepsilon^2}$$

Equation 19.18 for the covariance in this example becomes

$$u(A_1,A_2) = \frac{\partial A_1}{\partial N_B}\frac{\partial A_2}{\partial N_B}u^2(N_B) + \frac{\partial A_1}{\partial \varepsilon}\frac{\partial A_2}{\partial \varepsilon}u^2(\varepsilon)$$

The required sensitivity coefficients are found as follows.

$$\frac{\partial A}{\partial N_B} = \frac{-1}{t_B\,\varepsilon} \qquad \frac{\partial A}{\partial \varepsilon} = -\frac{N_S/t_S - N_B/t_B}{\varepsilon^2} = -\frac{A}{\varepsilon}$$

For the first measurement

$$A_1 = \frac{1210/3000 - 108/6000}{0.423} = 0.91095 \text{ Bq}$$

$$u_c(A_1) = \sqrt{\frac{1210/3000^2 + 108/6000^2}{0.423^2} + 0.91095^2\,\frac{0.012^2}{0.423^2}} = 0.0379 \text{ Bq}$$

$$\frac{\partial A_1}{\partial N_B} = \frac{-1}{(6000)(0.423)} = -3.9401 \times 10^{-4} \text{ Bq}$$

$$\frac{\partial A_1}{\partial \varepsilon} = -\frac{0.91095}{0.423} = -2.1536 \text{ Bq}$$

For the second measurement

$$A_2 = \frac{1244/3000 - 108/6000}{0.423} = 0.93775 \text{ Bq}$$

$$u_c(A_2) = \sqrt{\frac{1244/3000^2 + 108/6000^2}{0.423^2} + 0.93775^2\,\frac{0.012^2}{0.423^2}} = 0.0387 \text{ Bq}$$

$$\frac{\partial A_2}{\partial N_B} = \frac{-1}{(6000)(0.423)} = -3.9401 \times 10^{-4} \text{ Bq}$$

$$\frac{\partial A_2}{\partial \varepsilon} = -\frac{0.93775}{0.423} = -2.2169 \text{ Bq}$$

So, the covariance is estimated to be

$$u(A_1,A_2) = (-3.9401 \times 10^{-4})(-3.9401 \times 10^{-4})(108) + (-2.1536)(-2.2169)(0.012)^2$$
$$= 7.043 \times 10^{-4}\ \mathrm{Bq}^2$$

The estimated correlation coefficient is

$$r(A_1,A_2) = \frac{u(A_1,A_2)}{u(A_1)\,u(A_2)} = \frac{7.043 \times 10^{-4}}{(0.0379)(0.0387)} = 0.48\,.$$

19.4.5 Special Considerations for Nonlinear Models

19.4.5.1 Uncertainty Propagation for Nonlinear Models

The first-order uncertainty propagation formula tends to give better variance estimates when the function f is linear, because the formula is derived from a linear approximation of f (i.e., a first-order Taylor polynomial). Generally, obtaining a reliable estimate of $u_c^2(y)$ using the first-order formula requires (at least) that whenever f is nonlinear in one of the input quantities X_i, the relative uncertainty of the input estimate x_i must be small.[9] In radiochemistry, for example, this fact implies that the uncertainty of an instrument calibration factor, chemical yield, or test portion size should be kept small.

If all the input estimates x_i are uncorrelated and distributed symmetrically about their means, a better approximation of $u_c^2(y)$ may be made by including higher-order terms in the uncertainty propagation formula, as shown below.

$$u_c^2(y) = \sum_{i=1}^{N} \left(\frac{\partial f}{\partial x_i} \right)^2 u^2(x_i) + \sum_{i=1}^{N} \sum_{j=1}^{N} \left(\frac{1}{2} \left(\frac{\partial^2 f}{\partial x_i \partial x_j} \right)^2 + \frac{\partial f}{\partial x_i} \frac{\partial^3 f}{\partial x_i \partial x_j^2} \right) u^2(x_i)\, u^2(x_j) \qquad (19.19)$$

See also Section 5.1.2 of the *GUM*. In some cases, if the uncertainties of the input estimates are extremely large, even Equation 19.19 may be inadequate.

[9] The uncertainty propagation formula also provides finite estimates of variance in cases where, strictly speaking, the true variance is infinite or undefined. For example, if x has a normal or Poisson distribution, the variance of $1 / x$ is undefined, although the formula provides a finite estimate of it. On the other hand, if the relative standard uncertainty of x is small, the combined variance $u_c^2(1 / x)$ will almost always be consistent with observation, making the estimate useful in practice.

EXAMPLE 19.12 Suppose x and y are independent estimates of input quantities X and Y, respectively. Then the combined variance of the product $p = xy$ according to the first-order uncertainty propagation formula is

$$u_c^2(p) = y^2 u^2(x) + x^2 u^2(y)$$

For example, suppose $x = 5$, with $u(x) = 0.5$, and $y = 10$, with $u(y) = 3$. Then $p = 50$, and the first-order formula gives the combined standard uncertainty

$$u_c(p) = \sqrt{10^2 0.5^2 + 5^2 4^2} = 15.8$$

When higher-order terms are included,

$$u_c^2(p) = y^2 u^2(x) + x^2 u^2(y) + 0 \times u^4(x) + \frac{1}{2} u^2(x) u^2(y) + \frac{1}{2} u^2(y) u^2(x) + 0 \times u^4(y)$$
$$= y^2 u^2(x) + x^2 u^2(y) + u^2(x) u^2(y)$$

With numbers,

$$u_c(p) = \sqrt{10^2 0.5^2 + 5^2 3^2 + 0.5^2 3^2} = 15.9$$

Since 15.9 is only slightly greater than 15.8, in this example the first-order approximation appears adequate.

The combined variance of the quotient $q = x / y$ according to the first-order formula is

$$u_c^2(q) = \frac{u^2(x)}{y^2} + q^2 \frac{u^2(y)}{y^2}$$

Using the same values for x and y again, $q = 0.5$ and the first-order formula gives

$$u_c(q) = \sqrt{\frac{0.5^2}{10^2} + 0.5^2 \frac{3^2}{10^2}} = 0.158$$

When the higher-order terms are included,

$$\frac{\partial q}{\partial x} = \frac{1}{y} \qquad \frac{\partial^2 q}{\partial x^2} = 0 \qquad \frac{\partial^3 q}{\partial x^3} = 0$$

$$\frac{\partial q}{\partial y} = -\frac{x}{y^2} \qquad \frac{\partial^2 q}{\partial y^2} = \frac{2x}{y^3} \qquad \frac{\partial^3 q}{\partial y^3} = -\frac{6x}{y^4}$$

$$\frac{\partial^2 q}{\partial x\,\partial y} = -\frac{1}{y^2} \qquad \frac{\partial^3 q}{\partial x\,\partial y^2} = \frac{2}{y^3} \qquad \frac{\partial^3 q}{\partial y\,\partial x^2} = 0$$

$$u_c^2(q) = \frac{u^2(x)}{y^2} + q^2\frac{u^2(y)}{y^2} + 0 \times u^4(x) + \left(\frac{1}{2}\left(-\frac{1}{y^2}\right)^2 + \left(\frac{1}{y}\right)\left(\frac{2}{y^3}\right)\right) u^2(x)\,u^2(y)$$

$$+ \left(\frac{1}{2}\left(-\frac{1}{y^2}\right)^2 + 0\right) u^2(y)\,u^2(x) + \left(\frac{1}{2}\left(\frac{4x^2}{y^6}\right) + \left(-\frac{x}{y^2}\right)\left(-\frac{6x}{y^4}\right)\right) u^4(y)$$

$$= \frac{u^2(x)}{y^2}\left(1 + 3\frac{u^2(y)}{y^2}\right) + q^2\frac{u^2(y)}{y^2}\left(1 + 8\frac{u^2(y)}{y^2}\right)$$

With numbers,

$$u_c(q) = \sqrt{\frac{0.5^2}{10^2}\left(1 + 3\frac{3^2}{10^2}\right) + 0.5^2\frac{3^2}{10^2}\left(1 + 8\frac{3^2}{10^2}\right)} = 0.205$$

In this case, since 0.205 is substantially larger than 0.158, the first-order formula is inadequate.

If the standard uncertainty of y is much larger than 3 (in this case 30 % in relative terms), even the higher-order formula begins to fail here.

19.4.5.2 Bias due to Nonlinearity

As noted earlier, when the measurement model has the form $Y = f(X_1,X_2,\ldots,X_N)$ and the input estimates are $x_1, x_2, \ldots, x_N$, the output estimate is given by $y = f(x_1,x_2,\ldots,x_N)$. If the function, f, is nonlinear, the output estimate, y, may be a biased estimate of the value of the output quantity, Y, even if the model is correct and each of the input estimates, x_i, is an unbiased estimate of the associated input quantity (Ku, 1966).

For example, if the model is $Y = f(X) = X^2$ and X is an unbiased estimator for some quantity θ, then $Y = X^2$ is a biased estimator for the quantity θ^2. (I.e., the mean of the square is not equal to the square of the mean.) Since the variance of X is $V(X) = E(X^2) - E(X)^2$ and the mean of X is $E(X) = \theta$, the mean of Y in this case is given by

$$E(Y) = E(X^2) = E(X)^2 + V(X) = \theta^2 + V(X) \tag{19.20}$$

So, the bias of $Y = X^2$ as an estimator for θ^2 is equal to the variance of X. In metrology the true variance of the estimator X is unknown of course, but the bias of an output estimate, $y = x^2$, can be estimated by $u^2(x)$, the square of the standard uncertainty of the input estimate, x.

More generally, the portion of the bias of y associated with the nonlinearity of the model may be estimated, if necessary, by the formula

$$\text{Bias}(y) \approx \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}\frac{\partial^2 f}{\partial x_i \partial x_j}u(x_i,x_j) \tag{19.21}$$

In practice, Equation 19.21 is equivalent to the following (Ku, 1966).

$$\text{Bias}(y) \approx \frac{1}{2}\sum_{i=1}^{N}\frac{\partial^2 f}{\partial x_i^2}u^2(x_i) + \sum_{i=1}^{N-1}\sum_{j=i+1}^{N}\frac{\partial^2 f}{\partial x_i \partial x_j}u(x_i,x_j) \tag{19.22}$$

This bias is usually negligible in comparison to the combined standard uncertainty, $u_c(y)$, if the relative standard uncertainty of each input estimate is small. (These equations are based on an approximation of the function f by a second-order Taylor polynomial.)

Note that the bias calculated by Equations 19.21 and 19.22 may not represent the overall bias of the output estimate. It represents only the bias associated with nonlinearity of the mathematical model. If the input estimates are biased or the model is inexact, the overall bias may be different.

MARLAP does not recommend correcting the output estimate for the estimated bias due to non-linearity. Instead, the standard uncertainties of the input estimates should be kept small enough to make this portion of the bias negligible. For a typical radiochemical measurement model involving a net count rate divided by a denominator consisting of a product of factors such as the counting efficiency, test portion size, and chemical yield, this requirement means keeping the uncertainties of the counting times and all the factors in the denominator relatively small. The relative uncertainties of the raw counts may be large.

EXAMPLE 19.13 If x is an estimate of a positive quantity X, the bias of $y = 1 / x$ as an estimate of $1 / X$ may be approximated using Equation 19.22. Since y is a function of only one variable, the partial derivatives of y are the same as ordinary derivatives. The first derivative is $dy/dx = -x^{-2}$ and the second derivative is $d^2y/dx^2 = 2x^{-3}$. So, the bias due to nonlinearity can be estimated as $\text{Bias}(y) \approx (1/2)(2x^{-3})u^2(x) = u^2(x)/x^3$.

Suppose $x = 1.2$ and its standard uncertainty is 0.2. Then the calculated value of y is 1 / 1.2, or 0.833, and the estimated bias of y due to nonlinearity is $0.2^2 / 1.2^3 = 0.023$.

EXAMPLE 19.14 If x and y are uncorrelated, unbiased estimates of quantities X and Y, respectively, the bias of the product $z = xy$ as an estimate of XY is given approximately by

$$\text{Bias}(z) \approx \frac{1}{2}\left(\frac{\partial^2 z}{\partial x^2} u^2(x) + \frac{\partial^2 z}{\partial y^2} u^2(y) \right)$$

which equals zero, since $\partial^2 z / \partial x^2 = \partial^2 z / \partial y^2 = 0$. (In this case, it can be shown that the bias of z is exactly zero, not just approximately zero.)

EXAMPLE 19.15 If t is an estimate of the decay time T for a radionuclide whose decay constant is λ (assumed to have negligible uncertainty), the bias of the estimated decay factor $D = e^{-\lambda t}$ is given approximately by

$$\text{Bias}(D) \approx \frac{1}{2}\frac{\partial^2 D}{\partial t^2} u^2(t) = \frac{1}{2}\lambda^2 e^{-\lambda t} u^2(t)$$

and the relative bias is $\lambda^2 u^2(t) / 2$. For example, suppose the radionuclide is ^{228}Ac, which has a half-life of $T_{1/2} = 6.15$ h, and the decay time has a standard uncertainty of $u(t) = 2$ h (large for the sake of illustration). Then the decay constant λ equals $\ln(2) / 6.15 = 0.112707$ h^{-1}. The bias equation above implies that the relative bias of the decay factor D due to the uncertainty of t is approximately

$$\frac{\text{Bias}(D)}{D} \approx \frac{1}{2}\lambda^2 u^2(t) = \frac{1}{2}(0.112707)^2 (2)^2 = 0.025$$

or 2.5 %. Note that the relative bias of D is small if $u^2(t) / T_{1/2}^2$ is small. (In this example, $u^2(t) / T_{1/2}^2 = 2^2 / 6.15^2 = 0.1058$.)

19.4.6 Monte Carlo Methods

An alternative to uncertainty propagation is the use of computerized Monte Carlo methods to propagate not the uncertainties of input estimates but their distributions. Given assumed distributions for the input estimates, the method provides an approximate distribution for the output estimate, from which the combined standard uncertainty or an uncertainty interval may be derived. The joint working group responsible for the *GUM* is reported to be developing new guidance on the use of such methods. Monte Carlo methods may be particularly useful when the distribution of the result is not approximately normal. However, these methods are most effective when the model can be formulated in terms of independent input estimates.

19.5 Radiation Measurement Uncertainty

19.5.1 Radioactive Decay

Although it is impossible to know when an unstable nucleus will decay, it is possible to calculate the probability of decay during a specified time interval. The lifetime of the nucleus has an *exponential distribution*, which is a model for the life of any object whose expected remaining life does not change with age.

The exponential distribution is described by one parameter λ, which measures the expected fractional decay rate. This parameter λ is called the *decay constant* and equals $\ln(2) / T_{1/2}$, or approximately $0.693 / T_{1/2}$, where $T_{1/2}$ is the half-life of the radionuclide (sometimes denoted by $t_{1/2}$). The half-life is the same as the median of the exponential distribution.

The probability that an atom will survive until time t without decaying is equal to $e^{-\lambda t}$. Thus the probability of survival decreases exponentially with time. Consequently, when a large number of atoms of the same radionuclide are considered, the expected number of surviving atoms also decreases exponentially with time, as shown in Figure 19.2.

Since the probability that an atom survives until time t is equal to $e^{-\lambda t}$, it follows that the probability of decay during this time is $1 - e^{-\lambda t}$.

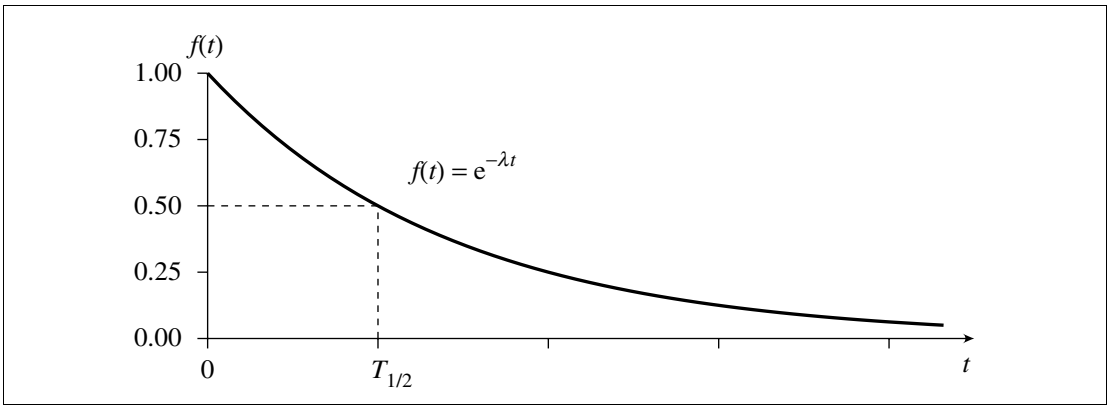

FIGURE 19.2 — Expected fraction of atoms remaining at time *t*

19.5.2 Radiation Counting

Undoubtedly the best-known rule of radiation measurement statistics is the fact that the counting uncertainty for a gross radiation measurement can be evaluated as the square root of the observed counts. The square-root rule is useful, because it permits the estimation of a potentially significant uncertainty component without replicate measurements. Although the rule is usually valid as an approximation, for reasons which are discussed below, there are limits to its applicability. It is also important to remember that the counting uncertainty is only one component of the total measurement uncertainty.

19.5.2.1 Binomial Model

When a source containing a radionuclide is placed in a detector, the probability that a particular atom of the radionuclide will produce a count is the product of three factors: the probability of decay, the probability of emission of the radiation being measured, and the probability of detection. According to the exponential decay model, the probability of decay is equal to $1 - e^{-\lambda t_S}$, where λ is the decay constant and t_S is the counting time. The probability of radiation emission, denoted here by F, is a characteristic of the radionuclide. The probability of detection is the counting efficiency, ε. Then the probability that an atom will generate a count is $p = (1 - e^{-\lambda t_S})F\varepsilon$.

If the source initially contains n atoms of the radionuclide, the instrument is stable, and its background is negligible, the number of observed counts N has a *binomial distribution with parameters n and p*. In general, if an experiment has only two possible outcomes, which may be called "success" and "failure," and the probability of success is p, then the number of successes observed when the experiment is repeated in n independent trials has a binomial distribution with parameters n and p.

Actually the probability p is a random variable, because the counting efficiency for an instrument and source can vary for a number of reasons, such as source placement, dead time and other instrument characteristics. These variations generate measurement uncertainty, but their effects are not included in the "counting uncertainty." The counting uncertainty is the standard deviation of the *theoretical* distribution of counts observed in a fixed time period when the efficiency is held constant. *Thus, the actual variability observed in repeated measurements of a single radioactive source may be greater than the theoretical counting uncertainty*.

19.5.2.2 Poisson Approximation

The mean and variance of the binomial distribution are np and $np(1 - p)$, respectively. In radiation counting, the value of p is usually small enough that the factor $1 - p$ in the variance can be ignored (i.e., treated as 1). When this is true, the binomial distribution can be approximated by a *Poisson distribution* with mean $\mu = np$. The variance of a Poisson distribution equals the mean; so, both can be estimated by the same measured result N, and the standard deviation can be estimated by $\sqrt{N}$.[10]

When μ is large, $\sqrt{N}$ is an excellent estimator for the standard deviation, σ_N, but the estimate may be poor when μ is small. For example, if $\mu = 100$, the coefficient of variation of $\sqrt{N}$ is only about 5 % and its bias (caused by the nonlinearity of the square-root function) is negligible.[11] If $\mu = 10$, the coefficient of variation is more than 16 % and there is a negative bias of more than 1 %. If $\mu = 1$, the coefficient of variation is more than 63 % and the negative bias is more than 22 %. Furthermore, when μ is small, it is possible to observe zero counts, so that $\sqrt{N} = 0$. MARLAP recommends that $\sqrt{N}$ be replaced by $\sqrt{N + 1}$ when extremely low counts are possible (see also Attachment 19D).[12]

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[10] In the rare cases when the Poisson model is inadequate and the binomial model is required, if the instrument background level is negligible, the standard deviation of the source count N_S can be estimated by $\sqrt{(1-p)N_S}$. If the background is not negligible, the variance of N_S is the sum of components contributed by the background and the source. So, if a Poisson background is measured for time t_B and N_B counts are observed, the background contribution to N_S is estimated by $N_B t_S / t_B$, and the source contribution is estimated by $(N_S - N_B t_S / t_B)$. Then the standard deviation of N_S may be estimated by combining the estimated variances of these two contributions, as shown below.

$$\sigma_{N_S} \approx \sqrt{N_B \frac{t_S}{t_B} + \left(N_S - N_B \frac{t_S}{t_B} \right) (1 - p)} = \sqrt{(1-p) N_S + p N_B \frac{t_S}{t_B}}$$

These expressions for the standard deviation of N_S are appropriate only when the source counts are generated by a single radionuclide or by one radionuclide plus the instrument background.

[11] The coefficient of variation of a nonnegative random variable is defined as the ratio of its standard deviation to its mean (see Attachment 19A).

[12] The negative bias of $\sqrt{N}$ as an estimator for σ_N is largely eliminated if one replaces it by $\sqrt{N + 0.25}$. MARLAP recommends the estimator $\sqrt{N + 1}$ although it is positively biased.

A sum of independent Poisson quantities also has a Poisson distribution. So, when the Poisson approximation is valid for all the sources of counts in a counting measurement, the total count obeys Poisson counting statistics as well.

If a short-lived radionuclide (large λ) is counted in a high-efficiency detector (large ε), the probability p that an atom placed in the detector will produce a count may be so large that the Poisson approximation is invalid. In this case the Poisson approximation overestimates the counting uncertainty; however, it is important to consider that the statistical model described thus far represents only the process of counting. In most cases previous steps in the measurement process decrease the probability that one of the atoms of interest initially present in the test portion (the portion of sample taken for analysis) will produce a count. If a correction for decay before counting is performed, the decay factor must be included in p. If the measured activity of a (single) decay product is used to estimate the activity of a parent, p must include both ingrowth and decay factors. If a chemical extraction is performed, the recovery factor must be considered. When these factors are included, the Poisson model is usually valid. Note, however, that these factors must be measured and their standard uncertainties evaluated and propagated, increasing the total measurement uncertainty even further.[13]

Both the binomial and Poisson models may be invalid if one atom can produce more than one count during the measurement. This situation occurs when the activity of a parent is estimated from the total count produced by the parent and a series of short-lived progeny (Lucas and Woodward, 1964; Collé and Kishore, 1997). For example when ^{222}Rn is measured by counting the emissions of the parent and its progeny, an atom of ^{222}Rn may produce several counts as it decays through the short-lived series ^{218}Po, ^{214}Pb, ^{214}Bi and ^{214}Po, to the longer-lived ^{210}Pb. Another example is the measurement of ^{234}Th by beta-counting a source that contains ^{234}Th and its short-lived progeny, ^{234m}Pa.

Both counting models may also be invalid if the total dead time of the measurement is significant (see Section 19.5.3.1).

Instrument background measurements are usually assumed to follow the Poisson model. This assumption is reasonable if the background counts are produced by low levels of relatively long-lived radionuclides. However, the true background may vary between measurements (e.g., cosmic background). Furthermore, the measured background may include spurious instrument-generated counts, which do not follow a Poisson distribution. Generally, the variance of the observed background is somewhat greater than the Poisson counting variance, although it may be

[13] It is possible to evaluate the uncertainties associated with the decay and ingrowth of a small number of short-lived atoms before counting using the binomial model, but under the stated conditions, the assumption of Poisson counting statistics simplifies the calculation. A more complete evaluation of uncertainty may be necessary if the same source is counted more than once.

less for certain types of instruments, such as those that use parallel coincidence counters to compensate for background instability (Currie et al., 1998). Departures from the Poisson model may be detected using the chi-squared test described in Section 18B.2 of Attachment 18B; however, deviations from the model over short time periods may be small and difficult to measure.

19.5.3 Count Time and Count Rate

Suppose a radiation counting measurement of duration t is made for the purpose of estimating a mean count rate r, assumed to be constant, and the result of the measurement (in counts) has a distribution that is approximately Poisson with mean rt. If t is known precisely, the best estimate of r given a single observation, N, is the measured count rate $R = N / t$, and the best estimate of the variance of the measured rate is $u^2(R) = N / t^2 = R / t$. Under the Poisson assumption, even if repeated measurements are made, the best estimates of the count rate and its variance are obtained by pooling the counts and count times and using the same formulas.

In fact, the count time t is known imperfectly; so a more complete estimate of the variance of R is

$$u^2(R) = \frac{N}{t^2} + \frac{N^2}{t^4} u^2(t) \tag{19.23}$$

The uncertainty of t may be ignored if $u(t) / t \ll 1 / \sqrt{N}$, that is, if the relative standard uncertainty of t is much less than 1 over the square root of the count.

EXAMPLE 19.16 A source is counted for $t = 100$ s, where t has standard uncertainty $u(t) = 0.1$ s, and $N = 25$ counts are observed. Thus, the observed count rate, R, equals 0.250 s^{-1}. When $u(t)$ is ignored, the combined standard uncertainty of R is $u_c(R) = \sqrt{N / t^2} = 0.050$ s^{-1}. When $u(t)$ is included, the combined standard uncertainty is

$$u_c(R) = \sqrt{\frac{N}{t^2} + \frac{N^2}{t^4} u^2(t)} = \sqrt{\frac{25}{100^2} + \frac{25^2}{100^4} 0.1^2} \approx 0.050 \text{ s}^{-1}$$

In this case the difference between the two uncertainty estimates is negligible.

EXAMPLE 19.17 A source is counted for $t = 100$ s, where $u(t) = 1$ s, and $N = 10{,}609$ counts are observed. The count rate, R, equals N / t, or 106.09 s^{-1}. When $u(t)$ is ignored, $u_c(R) = \sqrt{N / t^2} =$ 1.03 s^{-1}. When $u(t)$ is included,

$$u_c(R) = \sqrt{\frac{N}{t^2} + \frac{N^2}{t^4}u^2(t)} = \sqrt{\frac{10{,}609}{100^2} + \frac{10{,}609^2}{100^4}1^2} \approx 1.48 \text{ s}^{-1}$$

In this example the two uncertainty estimates are clearly different, although both are relatively small (1 % to 1.4 %).

Sometimes a radiation counter is set to acquire a predetermined number of counts. In this case the number of counts is a constant and only the count time varies. If the mean count rate does not change appreciably during the measurement, then Equation 19.23 may still be used.[14]

19.5.3.1 Dead Time

The *dead time* for a counting instrument is the minimum separation, τ, between two events required for the instrument to process and record both. Theoretical models for dead time are generally of two types. If the dead time for one event may be extended by a second event that arrives before the first has been processed, the system is called "paralyzable" and the dead time is called "extendable." Otherwise, the system is called "non-paralyzable" and the dead time is called "non-extendable" (Knoll, 1989; Turner, 1995; NCRP, 1985). Both models are idealized. The behavior of an actual counting system tends to fall between the two extremes. At low count rates, however, both models give essentially the same predictions.

At low count rates the observed count rate, N / t, may be corrected for dead time by dividing by the factor $1 - N\tau / t$. Many counting instruments perform the correction automatically by extending the real time t of the measurement to achieve a desired live time, t_L. Since $t_L = t - N\tau$, the corrected count rate is simply N / t_L. When the dead time rate for the measurement is low, the variance of the corrected count rate may be estimated as N / t_L^2. Thus, the Poisson model remains adequate if the "count time" is equated with the live time. When the dead time rate is high (above 20 %), the same estimate may not be adequate (NCRP, 1985). In this case the measurement should be repeated, if possible, in a manner that reduces the dead time rate.

Dead time effects may be evaluated experimentally to confirm that they do not invalidate the Poisson model at the count rates expected for typical measurements. The chi-squared test described in Section 18B.2 of Attachment 18B can be used for this purpose.

[14] If the mean count rate, r, is constant, the waiting times between events are independent exponentially distributed random variables with parameter $\lambda = r$. Therefore, the total time required to obtain n counts is the sum of the n waiting times, which has a *gamma distribution* with parameters $\alpha = n$ and $\lambda = r$ (or $\alpha = n$ and $\beta = 1/\lambda = 1/r$).

19.5.3.2 A Confidence Interval for the Count Rate

When the Poisson model of radiation counting is valid, lower and upper confidence limits for the mean count rate r given an observation of N counts in time t may be calculated as follows:[15]

$$r_{\text{lower}} = \chi^2_{(1-\gamma)/2}(2N) \,/\, 2t$$
$$r_{\text{upper}} = \chi^2_{(1+\gamma)/2}(2N + 2) \,/\, 2t \qquad (19.24)$$

Here γ is the desired *confidence coefficient*, or the minimum probability of coverage, and for any v, $\chi^2_p(v)$ denotes the p-quantile of the chi-squared distribution with v degrees of freedom (see Table G.3 in Appendix G). If $v = 0$, the chi-squared distribution $\chi^2(v)$ is degenerate. For our purposes, $\chi^2_p(0)$ should be considered to be 0.

EXAMPLE 19.18 Suppose 10 counts are observed during a 600-second instrument background measurement. Then the 95 % confidence limits for the background count rate are

$$r_{\text{lower}} = \frac{\chi^2_{0.025}(20)}{(2)(600)} = \frac{9.59078}{1200} = 0.00799 \text{ s}^{-1}$$
$$r_{\text{upper}} = \frac{\chi^2_{0.975}(22)}{(2)(600)} = \frac{36.7807}{1200} = 0.03065 \text{ s}^{-1}$$

EXAMPLE 19.19 Suppose 0 counts are observed during a 600-second measurement. Then the 95 % confidence limits for the count rate are

$$r_{\text{lower}} = \frac{\chi^2_{0.025}(0)}{(2)(600)} = 0 \text{ s}^{-1}$$
$$r_{\text{upper}} = \frac{\chi^2_{0.975}(2)}{(2)(600)} = \frac{7.3778}{1200} = 0.00615 \text{ s}^{-1}$$

[15] The chi-squared distribution is a special case of a gamma distribution, whose relationship to the Poisson distribution is described by Hoel et al. (1971) and Stapleton (1995). This relationship is the basis for the two formulas in Equation 19.24. The relationship is such that if X is chi-squared with $2N$ degrees of freedom and Y is Poisson with mean μ, then $\Pr[X \le 2\mu] = \Pr[Y \ge N]$.

19.5.4 Instrument Background

As noted above, single-channel background measurements are usually assumed to follow the Poisson model, although there may be effects which increase the variance beyond what the model predicts. For example, cosmic radiation and other natural sources of instrument background may vary between measurements, the composition of source holders and containers may vary, the instrument may become contaminated by sources, or the instrument may simply be unstable. For certain types of instruments, the Poisson model may overestimate the background variance (Currie et al., 1998). If the background does not closely follow the Poisson model, its variance should be estimated by repeated measurements.

The "instrument background," or "instrument blank," is usually measured with source holders or containers in place, since the presence of the container may affect the count rate. In many cases, perhaps most, it is not feasible to use the same container during both the background and test source measurements, but nearly identical containers should be used. Variations in container composition may affect the background count rate. If test sources contain enough mass to attenuate background radiation, then it is best to use a similar amount of blank material during the background measurement.

If repeated measurements demonstrate that the background level is stable, then the average, $\overline{x}$, of the results of many similar measurements performed over a period of time may give the best estimate of the background. In this case, if all measurements have the same duration, the experimental standard deviation of the mean, $s(\overline{x})$, is also a good estimate of the measurement uncertainty. Given the Poisson assumption, the best estimate of the uncertainty is still the Poisson estimate, which equals the square root of the summed counts, divided by the number of measurements, but the experimental standard deviation may be used when the Poisson assumption is invalid.

If the background drifts or varies nonrandomly over time (i.e., is nonstationary), it is important to minimize the consequences of the drift by performing frequent blank measurements.

If the background variance includes a small non-Poisson component, that component can be estimated from historical background data and added to the calculated Poisson component. A chi-squared statistic may be used to detect and quantify non-Poisson background variance (Currie, 1972; see also Section 18B.3 of Attachment 18B), but chi-squared provides an unbiased estimate of the additional variance only if the background remains stationary while the data are being collected. If the observed background counts, in order, are $N_1, N_2, \ldots, N_n$ and the corresponding counting intervals are $t_1, t_2, \ldots, t_n$, then the quantity

$$\xi_B^2 = \frac{1}{n-1}\sum_{i=1}^{n-1}\left[\left(\frac{N_{i+1}}{t_{i+1}} - \frac{N_i}{t_i}\right)^2 - \frac{N_i + N_{i+1}}{t_i t_{i+1}}\right] \tag{19.25}$$

may be used to estimate the non-Poisson variance of a net count rate due to background even if the background is not stationary.[16] The distribution of ξ_B^2 is not simple, and ξ_B^2 may even assume negative values, which are clearly unrealistic. So, if this estimator is used, it should be calculated for several data sets and for more than one instrument, if possible, to give an indication of its reliability. Although replicate measurements are involved, this type of evaluation of uncertainty should be considered a Type B method.

If background and test source measurements are performed under different conditions, the background measurement may be biased. Such a bias may occur, for example, if test sources are counted in containers or on planchets which are not present during background measurements. A situation of this kind should be avoided if possible.

When instrument background levels are low or when count times are short, it is possible that too few counts will be observed to provide an accurate estimate of the measurement uncertainty. Attachment 19D describes a method for choosing an appropriate coverage factor when only few counts are observed.

19.5.5 Radiochemical Blanks

Instrument background is only one of the sources of counts observed when an analyte-free sample is analyzed. Other sources may include contaminants in the tracers, reagents, and glassware used for measurements. Contamination of this type tends to be most significant when the analytes are naturally occurring radionuclides, such as isotopes of uranium, thorium, and radium; but nonnatural contaminants may also be present in some radiochemical tracers.

The level of contamination may be determined by analyzing reagent blanks or other process blanks alongside laboratory samples (see Chapter 18). Alternatively, if the contaminant is present in a specific reagent or tracer solution, its concentration in the solution may be measured and incorporated into the mathematical model of the measurement. Regardless of which method of evaluation is used, it is important to remember that the concentration of contaminant may vary from one reagent lot to another, and that the amount of contaminant in the prepared source may

[16] Each term of the sum is an unbiased estimator for the non-Poisson variance of the difference between successive measurements of the background. Note that $(N_{i+1}/t_{i+1} - N_i/t_i)^2$ is an unbiased estimator for the total variance and $(N_i + N_{i+1})/t_i t_{i+1}$, which equals $(N_i + N_{i+1})/(t_i + t_{i+1}) \times (1/t_i + 1/t_{i+1})$, is an unbiased estimator for the Poisson variance.

be affected by incomplete recovery during the chemical separation and purification steps of the analytical process.

If the amount of blank contaminant varies between measurements (e.g., because the analyte is present at varying levels in the laboratory environment), it is usually necessary to determine the blank level and its uncertainty by replicate measurements (a Type A evaluation). *In this case, using the pure Poisson model for the uncertainty of the blank correction is inappropriate*. Replicate measurements are also more appropriate if the causes of blank contamination are simply not well understood.

If there is no observable contamination when analyte-free samples are analyzed, the radiochemical blank may be only a blank source, which mimics the geometry and composition of an actual test source. In this case the laboratory should routinely analyze method blanks to check for contamination (see Chapter 18) and take corrective action if contamination is found.

19.5.6 Counting Efficiency

The counting efficiency for a measurement of radioactivity (usually defined as the detection probability for a particle or photon of interest emitted by the source) may depend on many factors, including source geometry, placement, composition, density, activity, radiation type and energy and other instrument-specific factors. The estimated efficiency is sometimes calculated explicitly as a function of such variables (in gamma-ray spectrometry, for example). In other cases a single measured value is used (e.g., alpha-particle spectrometry). If an efficiency function is used, the uncertainties of the input estimates, including those for both calibration parameters and sample-specific quantities, must be propagated to obtain the combined standard uncertainty of the estimated efficiency. Calibration parameters tend to be correlated; so, estimated covariances must also be included. If a single value is used instead of a function, the standard uncertainty of the value is determined when the value is measured.

EXAMPLE 19.20 Fifteen sources in the same geometry are prepared from a standard solution and used to calibrate a radiation counter. The specific activity of the standard is 150.0 Bq/g with a combined standard uncertainty of 2.0 Bq/g. The steps of the calibration are as follows:

1. A 1-milliliter aliquant of the standard solution is added by pipet to each source and weighed on an analytical balance. The solution contains the radionuclide of interest dissolved in 0.3 M nitric acid, whose density at the current room temperature is 1.0079 g/mL. The density of the solution is used only to calculate the buoyancy-correction factor for the mass measurements, which equals 1.001028 in this case (see Attachment 19E). The uncertainties of the buoyancy-corrected masses are considered negligible.

2. A blank measurement is made. The blank count time is 6000 s. The number of blank counts observed is 87.
3. Each source is counted once on the instrument for 300 s.

The radionuclide is long-lived; so, no decay corrections are needed. The uncertainties of the count times are assumed to be negligible.

The mathematical model for the calibration is:

$$\varepsilon = \frac{1}{n}\sum_{i=1}^{n}\frac{N_{S,i}/t_S - N_B/t_B}{m_i a_S}$$

where

ε	is the counting efficiency;
n	is the number of sources (15);
$N_{S,i}$	is the gross count observed during the measurement of the i^{th} source;
t_S	is the source count time (300 s);
N_B	is the observed blank count (87);
t_B	is the blank count time (6000 s);
m_i	is the mass of standard solution added to the i^{th} source; and
a_S	is the specific activity of the standard solution (150.0 Bq/g).

For the purpose of uncertainty evaluation, it is convenient to rewrite the model as

$$\varepsilon = \frac{\overline{R}}{a_S}$$

where

$$\overline{R} = \frac{1}{n}\sum_{i=1}^{N} R_i \qquad \text{and} \qquad R_i = \frac{N_{S,i}/t_S - N_B/t_B}{m_i}, \quad i = 1, 2, ..., n$$

The values R_i and their average, $\overline{R}$, are estimates of the count rate produced by 1 g of the standard solution, while $\overline{R}/a_S$ is an estimate of the count rate produced by 1 Bq of activity. The standard uncertainty of $\overline{R}$ can be evaluated experimentally from the 15 repeated measurements. Since only one blank measurement is made, the input estimates R_i are correlated with each other. The covariance between R_i and R_j, for $i \neq j$, may be estimated as

$$u(R_i, R_j) = \frac{\partial R_i}{\partial N_B}\frac{\partial R_j}{\partial N_B}u^2(N_B) = \frac{-1}{t_B m_i}\frac{-1}{t_B m_j}u^2(N_B) = \frac{u^2(N_B)}{t_B^2 m_i m_j}$$

However, the correlation is negligible here because the uncertainty of the blank count, N_B, is much smaller than the uncertainty of each source count, $N_{S,i}$. So, the input estimates R_i will be treated as if they were uncorrelated, and the following equations will be used to calculate the combined standard uncertainty of ε:

$$u^2(\overline{R}) = s^2(\overline{R}) = \frac{1}{n(n-1)} \sum_{i=1}^{n} (R_i - \overline{R})^2$$

$$u_c(\varepsilon) = \sqrt{\frac{u^2(\overline{R})}{a_S^2} + \varepsilon^2 \frac{u^2(a_S)}{a_S^2}}$$

Assume the following data were obtained for the 15 calibration sources.

Source number, i	Uncorrected mass (g)	Buoyancy-corrected mass, m_i / g	Gross count, $N_{S,i}$	R_i / ($s^{-1} \cdot g^{-1}$)
1	1.0056	1.00663	18,375	60.832
2	1.0031	1.00413	18,664	61.943
3	1.0058	1.00683	18,954	62.737
4	1.0082	1.00924	19,249	63.562
5	1.0069	1.00793	19,011	62.857
6	1.0074	1.00843	18,936	62.578
7	1.0048	1.00583	18,537	61.417
8	1.0069	1.00794	18,733	61.937
9	1.0031	1.00413	18,812	62.434
10	1.0079	1.00894	18,546	61.258
11	1.0063	1.00734	18,810	62.229
12	1.0067	1.00774	19,273	63.736
13	1.0055	1.00653	18,893	62.554
14	1.0091	1.01014	18,803	62.033
15	1.0030	1.00403	18,280	60.674
			Average, $\overline{R}$ / ($s^{-1} \cdot g^{-1}$):	62.1854
			Experimental standard deviation, $s(R_i)$ / ($s^{-1} \cdot g^{-1}$):	0.8910
			Experimental standard deviation of the mean, $s(\overline{R})$ / ($s^{-1} \cdot g^{-1}$):	0.2301

Then the estimated counting efficiency is

$$\varepsilon = \frac{\overline{R}}{a_S} = \frac{62.1854\ s^{-1} \cdot g^{-1}}{150.0\ Bq/g} = 0.4146$$

and the (combined) standard uncertainty of ε is given by

$$u(\varepsilon) = \sqrt{\frac{(0.2301\ \mathrm{s^{-1}\cdot g^{-1}})^2}{(150.0\ \mathrm{Bq/g})^2} + 0.4146^2 \times \frac{(2.0\ \mathrm{Bq/g})^2}{(150.0\ \mathrm{Bq/g})^2}} = 0.005736$$

which may be rounded to 0.0057. (Note that the relative standard uncertainty of ε is approximately 1.4 %, which is large enough to justify neglecting the small uncertainties of the masses.)

In fact the standard uncertainty of ε calculated in the preceding example may be incomplete. The true counting efficiency may vary from source to source because of variations in geometry, position and other influence quantities not explicitly included in the model. So, the standard uncertainty of ε should include not only the standard uncertainty of the estimated mean, as calculated in the example, but also another component of uncertainty due to variations of the true efficiency during subsequent measurements. The additional component may be written as $\varepsilon\varphi$, where φ is the coefficient of variation of the true efficiency. Then the total uncertainty of ε is obtained by squaring the original uncertainty estimate, adding $\varepsilon^2\varphi^2$, and taking the square root of the sum.

$$u(\varepsilon) = \sqrt{\frac{u^2(\overline{R})}{a_S^2} + \varepsilon^2\left(\frac{u^2(a_S)}{a_S^2} + \varphi^2\right)} \tag{19.26}$$

In the example above, the experimental variance of the ratios, R_i, may be used to estimate φ. Section 18B.2 of Attachment 18B, describes an approach for estimating such "excess" variance in a series of measurements. When the methods of Section 18B.2 are used with these data, the resulting estimate of φ is approximately 0.012, or 1.2 %. So, the total uncertainty of ε as a predictor of the counting efficiency for a source prepared and counted at some time in the future is

$$u(\varepsilon) = \sqrt{\frac{(0.2301\ \mathrm{s^{-1}\cdot g^{-1}})^2}{(150.0\ \mathrm{Bq/g})^2} + 0.4146^2\left(\frac{(2.0\ \mathrm{Bq/g})^2}{(150.0\ \mathrm{Bq/g})^2} + 0.012^2\right)} = 0.0076 \tag{19.27}$$

Variations in counting efficiency due to source placement should be reduced as much as possible through the use of positioning devices that ensure a source with a given geometry is always placed in the same location relative to the detector. If such devices are not used, variations in source position may significantly increase the measurement uncertainty.

Calibrating an instrument under conditions different from the conditions under which test sources are counted may lead to large uncertainties in the sample activity measurements. Source geometry in particular tends to be an important factor for many types of radiation counters. Generally, calibration sources should be prepared with the sizes and shapes of test sources and counted in the same positions, although in some cases it may be possible to calculate correction factors which allow one calibration to be used for different geometries. When correction factors are used, their uncertainties should be evaluated and propagated.

If the efficiency, ε, is calculated from a model that includes one of the quantities X_i appearing elsewhere in the sample activity model, there is a correlation between the measured values of ε and X_i, which should not be ignored. It is often simpler to include the entire expression for ε in the expression for the laboratory sample activity before applying the uncertainty propagation formula.

EXAMPLE 19.21 Suppose the counting efficiency for a measurement is modeled by the equation $\varepsilon = A \exp(-B m_S)$, where A and B are calibration parameters and m_S is the source mass; and suppose the chemical yield Y is modeled by m_S / m_C, where m_C is the expected mass at 100 % recovery. Then the estimated values of the counting efficiency and the yield are correlated, because both are calculated from the same measured value of the source mass. When the combined standard uncertainty of the sample activity is calculated, the covariance $u(\varepsilon, Y)$ may be included in the uncertainty propagation formula (see Section 19.4.4), or the variables ε and Y in the model may be replaced by the expressions $A \exp(-B m_S)$ and m_S / m_C, respectively, before the sensitivity coefficients are calculated.

In some cases the estimated value of the counting efficiency has *no effect* on the output estimate of laboratory sample activity. This happens often in alpha-particle spectrometry, for example, when isotopic tracers are used. The efficiency estimate is needed to obtain an estimate of the yield of the chemistry procedure, but the efficiency usually cancels out of the mathematical model for the laboratory sample activity and its uncertainty is not propagated when determining the combined standard uncertainty of the activity estimate.

19.5.7 Radionuclide Half-Life

The component of combined standard uncertainty associated with the half-life of a radionuclide is often negligible in measurements performed by typical radioanalytical laboratories, since the half-lives of most radionuclides of interest have been measured very accurately and in many cases decay times are short relative to the half-life (so that the sensitivity coefficient is small). However, this uncertainty component is also one of the most easily obtained components, since radionuclide half-lives and their standard uncertainties are evaluated and published by the National Nuclear Data Center (NNDC) at Brookhaven National Laboratory. The data may be obtained from the NNDC web site (www.nndc.bnl.gov).

19.5.8 Gamma-Ray Spectrometry

Most radiochemistry laboratories rely on commercial software for the analysis of gamma-ray spectra and for the evaluation and propagation of the associated uncertainties. There are a number of sources of measurement uncertainty in gamma-ray spectrometry, including:

- Poisson counting uncertainty;
- Compton baseline determination;
- Background peak subtraction;
- Multiplets and interference corrections;
- Peak-fitting model errors;
- Efficiency calibration model error;
- Summing;
- Density-correction factors; and
- Dead time.

See Chapter 16 for further discussion of measurement models and uncertainty analysis for gamma-ray spectrometry, but note that neither Chapter 16 nor this chapter attempts to describe all of the relevant issues in detail.

19.5.9 Balances

The uncertainty of a balance measurement tends to be small, even negligible, when the balance is used properly and the mass being measured is much larger than the balance's readability. However, the uncertainty may also be difficult to evaluate unless the balance is well maintained and operated in a controlled environment that protects it from external influences. In particular, drafts or sudden changes in pressure, temperature or humidity (e.g., opening doors or dishwashers) may produce spurious errors.

Even if one assumes the balance measurement uncertainty is negligible, there are reasons for performing at least a partial evaluation of the uncertainty. One reason is to confirm the assumption that the uncertainty is negligible or to determine the range of measurement conditions under which the assumption is true. For example the uncertainty may be significant if the mass being weighed is comparable in magnitude to the readability of the balance, or if the mass is calculated as the difference between two much larger and nearly equal masses that are determined at different times and under possibly different environmental conditions (e.g., a planchet and filter weighed before and after adding a small amount of precipitate to the filter). Another reason is to establish acceptance criteria for the strict quality control necessary to ensure that the uncertainty remains negligible.

The uncertainty of a mass measurement generally has components associated with

- Calibration;
- Linearity;
- Repeatability;
- Day-to-day or hour-to-hour variability due to environmental factors; and
- Air buoyancy.

Other sources of uncertainty may include leveling errors and off-center errors, which should be controlled. Static electrical charges may also have an effect. For some materials gain or loss of mass before or after weighing (e.g., by absorption or evaporation of water) may be significant. Attachment 19E of this chapter describes balance measurement uncertainties in more detail.

Balance manufacturers provide specifications for repeatability and linearity, which are usually of the same order of magnitude as the balance's readability, but tests of repeatability and linearity should also be included in the routine quality control for the balance.

Repeatability is expressed as a standard deviation, s_r, and is typically assumed to be independent of the load. It represents the variability of the result of zeroing the balance, loading and centering a mass on the pan, and reading the final balance indication. Attachment 19E describes procedures for evaluating the repeatability experimentally.

The linearity tolerance of a balance, a_L, should be specified by the manufacturer as the maximum deviation of the balance indication from the value that would be obtained by linear interpolation between the calibration points. Different methods may be used to convert this tolerance to a standard uncertainty, depending on the form the linearity error is assumed to take. One method, which is recommended by the *Eurachem/CITAC Guide: Quantifying Uncertainty in Analytical Measurement*, is to treat the tolerance, a_L, as the half-width of a rectangular distribution and divide a_L by $\sqrt{3}$ to obtain the standard uncertainty (Eurachem, 2000). Another method, suggested in Attachment 19E of this chapter, is to treat the linearity error as a sinusoidal function of the load, with amplitude a_L. This model requires that a_L be divided by $\sqrt{2}$ to obtain the standard uncertainty. The latter method is used below.

Procedures for evaluating the relative standard uncertainties due to calibration and environmental factors and for calculating the buoyancy-correction factor and its standard uncertainty are described in Attachment 19E.

When one evaluates the uncertainty of a balance measurement that is performed as part of a typical radiochemical measurement, where the relative combined standard uncertainty of the final result is usually 5 % or more, often much more, the evaluation may involve only a few components of the uncertainty. Important components for this purpose include those due to repeatability, linearity, and environmental factors. Gains or losses of mass may be important in some cases, but calibration errors and buoyancy effects usually can be ignored, since they tend to be significant in the mass measurement only when the total uncertainty of the mass is so small

that it is negligible in the overall analytical process. The remainder of this section will consider only the mass uncertainties due to repeatability, linearity, and environmental factors (but see Attachment 19E).

A typical mass measurement in the laboratory involves separate measurements of a gross mass and a tare mass. The net mass, m, is determined by subtracting the balance indication for the tare mass, I_{tare}, from the indication for the gross mass, I_{gross}. That is,

$$m = I_{\text{net}} = I_{\text{gross}} - I_{\text{tare}} \tag{19.28}$$

If the tare and gross measurements are made under the same environmental conditions (e.g., at nearly the same time), the standard uncertainty of m is given (according to the simplified model) by

$$u(m) = \sqrt{2s_{\text{r}}^2 + a_{\text{L}}^2 + m^2\varphi_{\text{env}}^2} \tag{19.29}$$

where

m is the net mass;
s_{r} is the repeatability standard deviation;
a_{L} is the linearity tolerance; and
φ_{env} is the relative standard uncertainty due to environmental effects.

In some cases the balance is simply zeroed before adding the mass and there is no tare measurement. (Unfortunately the operation of zeroing the balance is often called "taring.") In such cases the factor 2 that appears before s_{r}^2 in Equation 19.29 should be omitted.

If tare and gross measurements are made under possibly different environmental conditions (e.g., on different days), then the following expression should be used to account for the greater uncertainty due to environmental effects.

$$u(m) = \sqrt{2s_{\text{r}}^2 + a_{\text{L}}^2 + \left(I_{\text{tare}}^2 + I_{\text{gross}}^2\right)\varphi_{\text{env}}^2} \tag{19.30}$$

EXAMPLE 19.22 The chemical yield (recovery) for a strontium analysis is determined gravimetrically by weighing a stainless steel planchet before and after evaporating a strontium nitrate solution onto it, and then dividing the net mass by the predicted mass of strontium nitrate at 100 % yield. The balance has readability 0.0001 g. According to the manufacturer it has repeatability 0.00010 g and linearity 0.00020 g, and these values have been reasonably well confirmed by historical QC data. The analyst has also used balance QC data to determine that the relative standard uncertainty due to environmental effects is approximately 2×10^{-5} (see Attachment 19E). Suppose for a particular measurement the tare mass of the planchet is 8.5923 g and the gross mass, which is measured two hours later, is 8.5978 g. Then the net mass is

$$m = 8.5978\ \text{g} - 8.5923\ \text{g} = 0.0055\ \text{g}$$

Since two hours elapse between the tare and gross measurements, Equation 19.30 is used to calculate the standard uncertainty.

$$\begin{aligned} u(m) &= \sqrt{2 s_r^2 + a_L^2 + \left(I_{tare}^2 + I_{gross}^2\right) \varphi_{env}^2} \\ &= \sqrt{2\,(0.00010\ \text{g})^2 + (0.00020\ \text{g})^2 + \left((8.5923\ \text{g})^2 + (8.5978\ \text{g})^2\right)(2 \times 10^{-5})^2} \\ &= 0.00035\ \text{g} \end{aligned}$$

Thus the relative standard uncertainty is approximately 6 %, which is significant in the determination of a yield factor.

Note that using the linearity tolerance, 0.00020 g, is rather conservative when the difference between the gross and tare masses is so small, but the uncertainty component due to linearity is not dominant in this example. It is actually smaller than the uncertainty due to environmental effects.

EXAMPLE 19.23 An aliquant of dry soil is subsampled for analysis and weighed on the same laboratory balance described in the preceding example. The repeatability of the balance is 0.00010 g, the linearity is 0.00020 g, and the relative standard uncertainty due to environmental effects is 2×10^{-5}. Suppose the analyst zeros the balance with an empty container on the pan, adds the aliquant of soil to the container, and reads the final balance indication without a significant time delay. If the final indication is 1.0247 g, then the mass estimate is m = 1.0247 g and its standard uncertainty is

$$\begin{aligned} u(m) &= \sqrt{s_r^2 + a_L^2 + m^2 \varphi_{Env}^2} \\ &= \sqrt{(0.00010\ \text{g})^2 + (0.00020\ \text{g})^2 + (1.0247\ \text{g})^2 (2 \times 10^{-5})^2} \\ &= 0.00022\ \text{g} \end{aligned}$$

So, the relative standard uncertainty is approximately 0.022 %, which is likely to be negligible in comparison to the uncertainty of subsampling (heterogeneity).

Note that in this example the uncertainty due to environmental effects is the smallest of the three uncertainty components.

19.5.10 Pipets and Other Volumetric Apparatus

Generally, a pipet or volumetric flask is used not to measure an existing volume of liquid, but to obtain a volume of a predetermined nominal size. The nominal value is treated as if it were a measured value, although it is known before the "measurement." The true volume is the variable quantity. Since a volumetric "measurement" of this type cannot be repeated, pipets and flasks are good examples of measurement systems for which historical data are important for Type A evaluations of standard uncertainty.

The uncertainty of a pipet measurement, like that of a balance measurement, is often relatively small in comparison to other uncertainties in a radiochemical analysis. However, the use of the wrong type of pipetting device for a particular measurement may result in a relatively large pipetting uncertainty. For example, one manufacturer's technical specifications for various models of pipetting devices list precision values that range from 0.1 % to 5 % and bias tolerances that range from 0.3 % to 12 %. (Here a "bias tolerance" means an upper bound for the possible magnitude of the pipet's unknown systematic error.) So, it is important for the user of a particular model to know its performance characteristics.

The total uncertainty of a volumetric measurement may include several components, but since most of the components are negligible in a typical radiochemical measurement process, a very simple method of evaluation is usually adequate as long as quality control is strict enough to ensure that the measuring devices and personnel are performing as expected. The method suggested here considers only two components, which are associated with precision and the capacity (or bias) of the device. Attachment 19E presents more complete methods of evaluation.

Any volumetric measuring device should have a specified tolerance for its capacity, or for the possible bias of the device (e.g., ASTM E288 and ASTM E969). This tolerance, δ_{cap}, may be assumed to represent the half-width of a rectangular or triangular distribution. Assuming a triangular distribution, as recommended by the Eurachem/CITAC Guide, one evaluates the uncertainty component of the volume associated with the capacity as $\delta_{cap} / \sqrt{6}$ (Eurachem, 2000).

The simplest type of uncertainty evaluation is possible when the manufacturer of a pipetting device provides specifications for both bias and precision (e.g., Eppendorf® pipettes). In this case the Type B standard uncertainty of a pipetted volume, V, may be evaluated as

$$u(V) = \sqrt{s^2 + \frac{\delta_{cap}^2}{6}} \tag{19.31}$$

where δ_{cap} is the manufacturer's stated bias tolerance and s is the stated standard deviation.

EXAMPLE 19.24 Suppose the manufacturer of a 5-milliliter pipetting device specifies the relative bias tolerance to be 0.6 % and the relative precision to be 0.2 %. Then the standard uncertainty of the volume may be evaluated as

$$u(V) = \sqrt{s^2 + \frac{\delta_{cap}^2}{6}} = \sqrt{(5\text{ mL} \times 0.002)^2 + \frac{(5\text{ mL} \times 0.006)^2}{6}} = 0.0158\text{ mL}$$

The relative standard uncertainty in this case is only about 0.3 %, which might be considered negligible for many applications.

EXAMPLE 19.25 Suppose the relative bias tolerance for an adjustable-volume pipetting device is 2.5 % when the device is set at 10 µL, and the relative precision is 0.7 %. Then the standard uncertainty of a volume delivered at the 10-microliter setting may be evaluated as

$$u(V) = \sqrt{s^2 + \frac{\delta_{cap}^2}{6}} = \sqrt{(10\text{ µL} \times 0.007)^2 + \frac{(10\text{ µL} \times 0.025)^2}{6}} = 0.124\text{ µL}$$

The relative standard uncertainty in this case is about 1.2 %, which would be considered potentially significant for many types of measurements.

When volumetric glassware is used, or when the manufacturer does not specify the precision, the uncertainty due to imprecision must be determined by other means. One Type B method of evaluating the imprecision for volumetric glassware is to examine the dimensions of the glassware and use experience and professional judgment to estimate the maximum possible deviation of the meniscus from the capacity line. If δ_{men} denotes this maximum deviation and d denotes the internal diameter of the glassware at the capacity mark, the maximum deviation of the volume from its value at the capacity mark is given by $\pi\delta_{men}d^2/4$. Note that if δ_{men} and d are expressed in centimeters, this expression gives a value in milliliters. Then, if δ_{men} is assumed to be the half-width of a triangular distribution, the standard uncertainty of V is given by the following equation

$$u(V) = \sqrt{\frac{\delta_{cap}^2 + (\pi\delta_{men}d^2/4)^2}{6}} \qquad (19.32)$$

A Type A (experimental) method of evaluation may also be used (see Attachment 19E).

EXAMPLE 19.26 Suppose the inside diameter of an ASTM Class-A 1-milliliter volumetric pipet is 0.4 cm, and the analyst estimates δ_{men}, the maximum deviation from the capacity line, to be 0.075 cm. The capacity tolerance, δ_{cap}, is specified by ASTM E969 to be 0.006 mL. So, the standard uncertainty of the volume (V = 1 mL) is

$$u(V) = \sqrt{\frac{\delta_{cap}^2 + (\pi \delta_{men} d^2 / 4)^2}{6}}$$

$$= \sqrt{\frac{(0.006\ \text{mL})^2 + (\pi\,(0.075\ \text{cm})\,(0.4\ \text{cm})^2 / 4)^2}{6}}$$

$$= 0.00456\ \text{mL}$$

The relative standard uncertainty is approximately 0.5 %.

19.5.11 Digital Displays and Rounding

If a measuring device, such as an analytical balance, has a digital display with resolution δ, the standard uncertainty of a measured value is at least $\delta / 2\sqrt{3}$. This uncertainty component exists even if the instrument is completely stable.

A similar Type B method may be used to evaluate the standard uncertainty due to computer roundoff error. When a value x is rounded to the nearest multiple of 10^n, the component of uncertainty generated by roundoff error is $10^n / 2\sqrt{3}$. When rounding is performed properly and x is printed with an adequate number of figures, this component of uncertainty should be negligible in comparison to the total uncertainty of x.

EXAMPLE 19.27 The readability of a digital balance is 0.1 g. Therefore, the minimum standard uncertainty of a measured mass is $0.1 / 2\sqrt{3} = 0.029$ g.

EXAMPLE 19.28 A computer printout shows the result x of a measurement as

```
3.40E+01 +- 9.2E-02
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where the expanded uncertainty is calculated using a coverage factor of 2. Since the coverage factor is 2, the printout implies the standard uncertainty is 0.092 / 2, or 0.046. However, since the measured value is rounded to the nearest multiple of 0.1, the standard uncertainty of x should be increased from 0.046 to

$$u(x) = \sqrt{0.046^2 + \left(\frac{0.1}{2\sqrt{3}}\right)^2} = 0.054\,.$$

19.5.12 Subsampling

Appendix F of this manual discusses laboratory subsampling. The subsampling of heterogeneous materials for laboratory analysis increases the variability of the measurement result and thus adds a component of measurement uncertainty, which is usually difficult to quantify without replicate measurements. Appendix F summarizes important aspects of the statistical theory of particulate sampling and applies the theory to subsampling in the radiation laboratory (see also Gy, 1992, and Pitard, 1993). The mathematical estimates obtained using the theory often require unproven assumptions about the material analyzed and rough estimates of unmeasurable parameters. However, in some cases the theory can be used to suggest how subsampling errors may be affected by either changing the subsample size or grinding the material before subsampling. Of course the total measurement uncertainty, including components contributed by subsampling, may always be evaluated by repeated subsampling and analysis.

If subsampling is not repeated, its effects may be represented in the mathematical measurement model by including an input quantity F_S whose value is the ratio of the analyte concentration of the subsample to that of the total sample. This ratio, which will be called the *subsampling factor* (a MARLAP term), appears in the model as a divisor of the net instrument signal and thus is similar to the chemical yield, counting efficiency and other sensitivity factors. The value of F_S is estimated as 1, but the value has a standard uncertainty, $u(F_S)$, which increases the combined standard uncertainty of the result.

Although the component of uncertainty caused by the subsampling of heterogeneous solid matter may be difficult to estimate, it should not be ignored, since it may be relatively large and in some cases may even dominate all other components. One may use previous experience with similar materials to evaluate the uncertainty, possibly with the aid of the information and methods presented in Appendix F. Appendix F shows how the value of the subsampling uncertainty depends on the maximum particle diameter, d, the mass of the sample, m_L, and the mass of the subsample, m_S. The equation for the standard uncertainty of F_S typically has the form

$$u(F_S) = \sqrt{\left(\frac{1}{m_S} - \frac{1}{m_L}\right) k d^3} \qquad (19.33)$$

where the value of k depends on the sample. By default, if "hot particles" are not suspected, and if reasonable precautions are taken either to homogenize (mix) the material or to build the subsample from a large number of randomly selected increments, one may assume $k \approx 0.4$ g/cm^3, or

0.0004 g/mm^3. If hot particles are suspected, special measurement techniques are probably required, as described in Appendix F. In this case Equation 19.33 should not be used.

EXAMPLE 19.29

Problem: A 609-gram soil sample is ground until it passes through an ASTM #10 sieve, which has a mesh size of 2.0 mm. The sample is then homogenized and a 0.7957-gram subsample is removed. Use Equation 19.33 with $k = 0.0004$ g/mm^3 to evaluate the standard uncertainty of the subsampling factor, $u(F_S)$. Repeat the evaluation assuming an ASTM #18 sieve, whose mesh size is 1.0 mm.

Solution: First, assume $d = 2.0$ mm. Then the subsampling uncertainty is

$$u(F_S) = \sqrt{\left(\frac{1}{0.7957\ \text{g}} - \frac{1}{609\ \text{g}}\right)(0.0004\ \text{g/mm}^3)(2.0\ \text{mm})^3} = 0.063$$

Now assume $d = 1.0$ mm. Then

$$u(F_S) = \sqrt{\left(\frac{1}{0.7957\ \text{g}} - \frac{1}{609\ \text{g}}\right)(0.0004\ \text{g/mm}^3)(1.0\ \text{mm})^3} = 0.022$$

Another alternative is to evaluate the subsampling variance for each type of material and analyte at a specified maximum particle size, d, and subsample mass, m_S. Such an evaluation can be performed experimentally by repeated subsampling and analysis of one or more actual samples, provided that the concentrations are high enough and the measurement precision good enough to allow estimation of the variance attributable to subsampling. However, an artificially spiked sample is usually inappropriate for this purpose, because its heterogeneity differs from that of real samples. If the precision of the measurement process after subsampling is inadequate, the subsampling variance may be hard to quantify experimentally.

19.5.13 The Standard Uncertainty for a Hypothetical Measurement

MARLAP's recommended method selection criteria in Chapter 3 require that a laboratory estimate the standard uncertainty for a measurement of the activity concentration of a radionuclide in a hypothetical laboratory sample whose true concentration is specified (i.e., the "method uncertainty," as defined by MARLAP). To estimate the combined standard uncertainty of the measured concentration, one must obtain estimates for all the input quantities and their standard uncertainties. All quantities except the gross instrument signal may be measured and the standard uncertainties evaluated by routine Type A and Type B methods. Alternatively, the values and

their standard uncertainties may be determined from historical data. The estimate of the gross signal and its standard uncertainty must be obtained by other means, since the laboratory sample is only hypothetical. The predicted value of the gross count N_S is calculated by rearranging the equation or equations in the model and solving for N_S. The standard uncertainty of the measured value may then be evaluated either from theory (e.g., Poisson counting statistics), historical data, or experimentation.

EXAMPLE 19.30 Suppose the mathematical model for a radioactivity measurement is

$$a = \frac{N_S/t_S - N_B/t_B}{m_S Y \varepsilon e^{-\lambda(t_D + t_S/2)} F_S}$$

where

a	is the specific activity of the radionuclide in the sample;
N_S	is the test source count;
N_B	is the blank count;
t_S	is the source count time;
t_B	is the blank count time;
t_D	is the decay time;
m_S	is the mass of the test portion;
Y	is the chemical yield;
ε	is the counting efficiency;
λ	is the decay constant; and
F_S	is the subsampling factor.

With values given for the specific activity a; test portion mass m_S; blank count N_B; count times t_S, t_B, and t_D; efficiency ε; and yield Y; the source count N_S can be predicted. The predicted value is $N_S = t_S\,(a m_S Y \varepsilon \exp(-\lambda(t_D + t_S/2)) + N_B/t_B)$. When this value is treated like a measured value, its estimated variance according to Poisson statistics is $u^2(N_S) = N_S$. So, assuming negligible uncertainties in the times t_S, t_B, and t_D, the (first-order) uncertainty propagation formula gives the combined variance of the output estimate, a, as

$$u_c^2(a) = \frac{u^2(N_S)/t_S^2 + u^2(N_B)/t_B^2}{m_S^2 Y^2 \varepsilon^2 e^{-2\lambda(t_D + t_S/2)}} + a^2\left(\frac{u^2(m_S)}{m_S^2} + \frac{u^2(Y)}{Y^2} + \frac{u^2(\varepsilon)}{\varepsilon^2} + \frac{u^2(F_S)}{F_S^2}\right)$$

$$= \frac{(a m_S Y \varepsilon e^{-\lambda(t_D + t_S/2)} + N_B/t_B)/t_S + N_B/t_B^2}{m_S^2 Y^2 \varepsilon^2 e^{-2\lambda(t_D + t_S/2)}} + a^2\left(\frac{u^2(m_S)}{m_S^2} + \frac{u^2(Y)}{Y^2} + \frac{u^2(\varepsilon)}{\varepsilon^2} + \frac{u^2(F_S)}{F_S^2}\right)$$

19.6 References

This section contains a combined list of references for Chapter 19 and its attachments.

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ATTACHMENT 19A
Statistical Concepts and Terms

19A.1 Basic Concepts

Every laboratory measurement involves a measurement error. Methods for analyzing measurement error are generally based on the theory of random variables. A *random variable* may be thought of as the numerical outcome of an experiment, such as a laboratory measurement, which produces varying results when repeated. In this document a random variable is most often the result of a measurement. Random variables will usually be denoted in this attachment by uppercase letters.

Of primary importance in almost any discussion of a random variable is its *distribution*, or *probability distribution*. The distribution of a random variable X describes the possible values of X and their probabilities. Although the word "distribution" has a precise meaning in probability theory, the term will be used loosely in this document. This attachment describes several types of distributions, including the following:

- normal (Gaussian)
- log-normal (or lognormal)
- chi-squared (or chi-square)
- Student's t
- rectangular (uniform)
- trapezoidal
- exponential
- binomial
- Poisson

Normal distributions are particularly important because they appear often in measurement processes. The other types listed are also important in this chapter, but only the exponential, binomial and Poisson distributions are described in the text.

The distribution of X is uniquely determined by its *distribution function*, defined by $F(x) = \Pr[X \le x]$, where $\Pr[X \le x]$ denotes the probability that X is less than or equal to x. The distribution function is also called the *cumulative distribution function* (cdf). If there is a function $f(x)$ such that the probability of any event $a \le X \le b$ is equal to $\int_a^b f(x)\,dx$ (i.e., the area under the curve $y = f(x)$ between $x = a$ and $x = b$), then X is a *continuous* random variable and $f(x)$ is a *probability density function* (pdf) for X. When X is continuous, the pdf uniquely describes its distribution. A plot of the pdf is the most often used graphical illustration of the distribution (e.g., see Figures 19.3 and 19.4), because the height of the graph over a point x indicates the probability that the value of X will be near x.

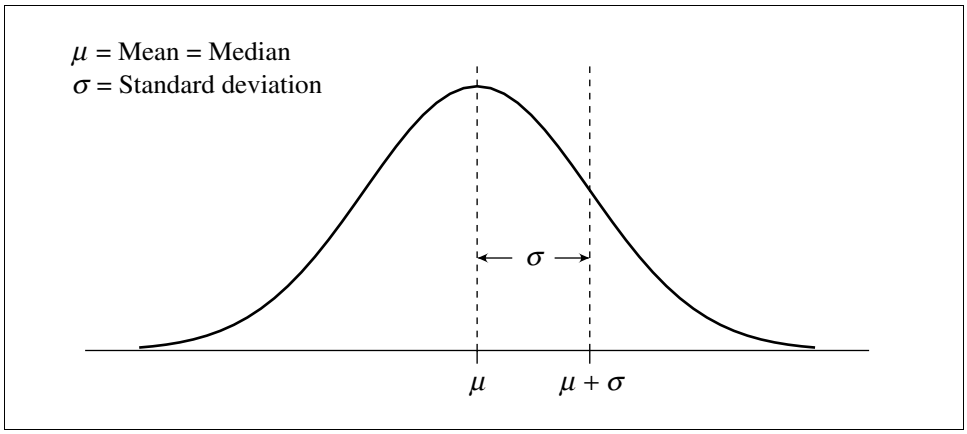

FIGURE 19.3 — A symmetric distribution

Two useful numerical characteristics of the distribution of a random variable are its *mean* and *variance*. The mean is also called the *expectation* or the *expected value* and may be denoted by μ_X or $E(X)$. The mean of a distribution is conceptually similar to the center of mass of a physical object. It is essentially a weighted average of all the possible values of X, where the weight of a value is determined by its probability. The variance of X, denoted by σ_X^2, Var(X), or $V(X)$, is a measure of the variability of X, or the dispersion of its values, and is defined as the expected value of $(X - \mu_X)^2$.

The *standard deviation* of X, denoted by σ_X is defined as the positive square root of the variance. Although the variance appears often in statistical formulas, the standard deviation is a more intuitive measure of dispersion. If X represents a physical quantity, then σ_X has the same physical dimension as X. The variance σ_X^2, on the other hand, has the dimension of X squared.

Any numerical characteristic of a distribution, such as the mean or standard deviation, may also be thought of as a characteristic of the random variables having that distribution.

The mean and standard deviation of a distribution may be estimated from a random sample of observations of the distribution. The estimates calculated from observed values are sometimes called the *sample mean* and *sample standard deviation*. Since the word "sample" here denotes a statistical sample of observations, not a physical sample in the laboratory, metrologists often use the terms *arithmetic mean, or average,* and *experimental standard deviation* to avoid confusion.

The mean is only one measure of the center of a distribution ("measure of central tendency"). Another is the median. The *median* of X is a value $x_{0.5}$ that splits the range of X into upper and lower portions which are equally likely, or, more correctly, a value $x_{0.5}$ such that the probability that $X \leq x_{0.5}$ and the probability that $X \geq x_{0.5}$ are both at least 0.5. Note that for some distributions the median may not be unique. Figure 19.4 shows the probability density function of a symmetric

distribution, whose mean and median coincide, and Figure 19.4 shows the pdf of an asymmetric distribution, whose mean and median are distinct.

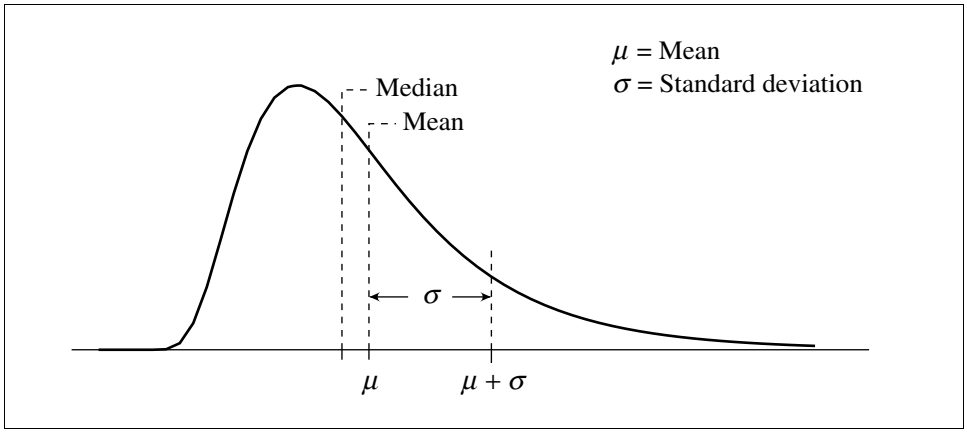

FIGURE 19.4 — An asymmetric distribution

The median of X is also called a *quantile of order* 0.5, or a 0.5-*quantile*. In general, if p is a number between 0 and 1, a p-quantile of X is a number x_p such that the probability that $X < x_p$ is at most p and the probability that $X \leq x_p$ is at least p. A p-quantile is often called a $100p^{\text{th}}$ *percentile*.

Sometimes the standard deviation of a nonnegative quantity is more meaningful when expressed as a fraction of the mean. The *coefficient of variation*, or CV, is defined for this reason as the standard deviation divided by the mean. The coefficient of variation is a dimensionless number, which may be converted to a percentage. The term "relative standard deviation," or RSD, is also used. The term "relative variance" is sometimes used to mean the square of the relative standard deviation.

The results of two analytical measurements may be *correlated* when they have measurement errors in common. This happens, for example, if laboratory samples are analyzed using the same instrument without repeating the instrument calibration. Any error in the calibration parameters affects all results obtained from the instrument. This type of association between two quantities X and Y is measured by their *covariance*, which is denoted by $\sigma_{X,Y}$ or $\text{Cov}(X,Y)$. The covariance of X and Y is defined as the expected value of the product $(X - \mu_X)(Y - \mu_Y)$.

Covariance, like variance, is somewhat nonintuitive because of its physical dimension. Furthermore, a large value for the covariance of two variables X and Y does not necessarily indicate a strong correlation between them. A measure of correlation must take into account not only the covariance $\sigma_{X,Y}$, but also the standard deviations σ_X and σ_Y. The *correlation coefficient*, denoted by $\rho_{X,Y}$, is therefore defined as $\sigma_{X,Y}$ divided by the product of σ_X and σ_Y. It is a dimensionless number between -1 and $+1$. The quantities X and Y are said to be strongly correlated when the absolute value of their correlation coefficient is close to 1.

Statistical formulas are generally simpler when expressed in terms of variances and covariances, but the results of statistical analyses of data are more easily understood when presented in terms of standard deviations and correlation coefficients.

The lack of a correlation between two quantities X and Y is not a sufficient condition to guarantee that two values $f(X)$ and $g(Y)$ calculated from them will also be uncorrelated. A stronger condition called *independence* is required. For most practical purposes, to say that two quantities are "independent" is to say that their random components are completely unrelated. A more rigorous definition appears in the MARLAP glossary.

When the value of a random variable X is used to estimate the value of an unknown parameter θ, then X is called an *estimator* for θ. The *bias* of X is the difference between the mean μ_X and the actual value θ. If the bias is zero, then X is said to be *unbiased*; otherwise, X is *biased*. Note that metrologists use the term "bias" with a somewhat different but similar meaning (see Section 19.3.1).

As mentioned in Section 19.4.5.2, even if X is an unbiased estimator for θ, the application of a nonlinear function, f, to X may produce a biased estimator, $f(X)$, for the value of $f(\theta)$. Colloquially speaking, the function of the mean is different from the mean of the function. For example, if X is an unbiased estimator for θ, then generally X^2 is a biased estimator for θ^2.

If the value of X is used not to estimate the value of a parameter but to "predict" the value of another random variable, Y, whose value oftentimes is not directly observed, then X is called a *predictor* for Y.

19A.2 Probability Distributions

This section briefly describes the probability distributions used in Chapter 19.

Distributions may be classified according to their mathematical properties. Distributions in the same class or family are described by the same mathematical formulas. The formulas involve numerical parameters which distinguish one member of the class from another.

Two important kinds of distributions are the normal and log-normal, which are observed often in nature. Other types of distributions important in radioanalysis include the rectangular, binomial, Poisson, Student's t, chi-squared and exponential distributions. Poisson distributions in particular are important in radiation counting measurements and are described in Section 19.5.2.

19A.2.1 Normal Distributions

Many quantities encountered in nature and in the laboratory have distributions which can be described by the "bell curve." This type of distribution, called a *normal*, or *Gaussian*, distribution, is usually a reasonably good model for the result of a radioanalytical measurement. A number of commonly used methods for evaluating data sets depend on their having an approximately normal distribution. The probability density function (pdf) for a normal distribution is shown in Figure 19.5.

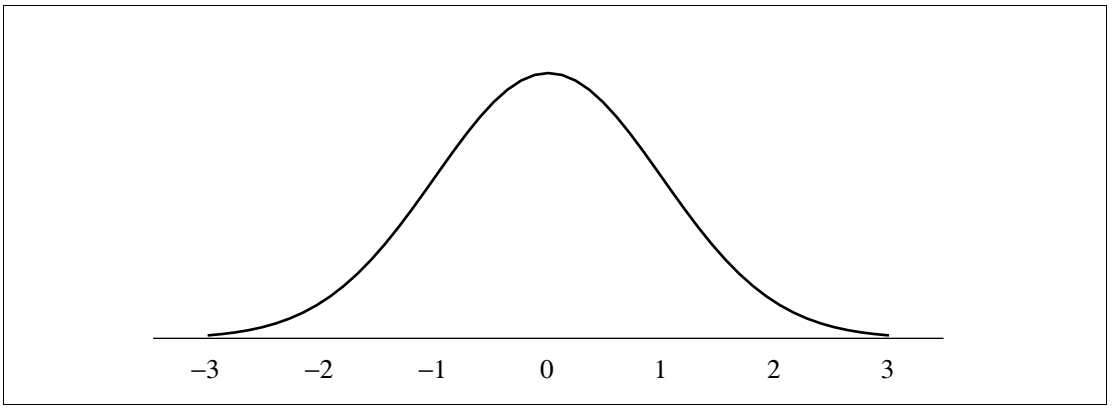

FIGURE 19.5 — A normal distribution

A normal distribution is uniquely specified by its mean μ and variance σ^2. The normal distribution with mean 0 and variance 1 is called the *standard normal distribution*. If X is normally distributed with mean μ and variance σ^2, then $(X - \mu) / \sigma$ has the standard normal distribution.

The sum of a large number of independent random variables has an approximately normal distribution, even if the individual variables themselves are not normally distributed, so long as the variance of each term is much smaller than the variance of the sum.[17] This is one reason why the normal distribution occurs often in nature. When a quantity is the result of additive processes involving many small random variations, the quantity tends to be normally distributed. It is also true that many other distributions, such as the binomial, Poisson, Student's t and chi-squared, can be approximated by normal distributions under certain conditions.

The mean value of a normal distribution is also its median, or the value that splits the range into equally likely portions.

[17] The number of quantities required to obtain a sum that is approximately normal depends on the distribution of the quantities. If the distribution is symmetric and mound-shaped like the bell curve, the number may be rather small. Other distributions such as the log-normal distribution, which is asymmetric, may require a much larger number.

The value of a normally distributed quantity will be within one standard deviation of the mean about 68 % of the time. It will be within two standard deviations about 95 % of the time and within three standard deviations more than 99 % of the time. It is important to remember that these percentages apply only to normal distributions.

19A.2.2 Log-normal Distributions

The concentration of a contaminant in the environment may not be normally distributed. Instead it often tends to be *log-normally* distributed, as shown in Figure 19.6.

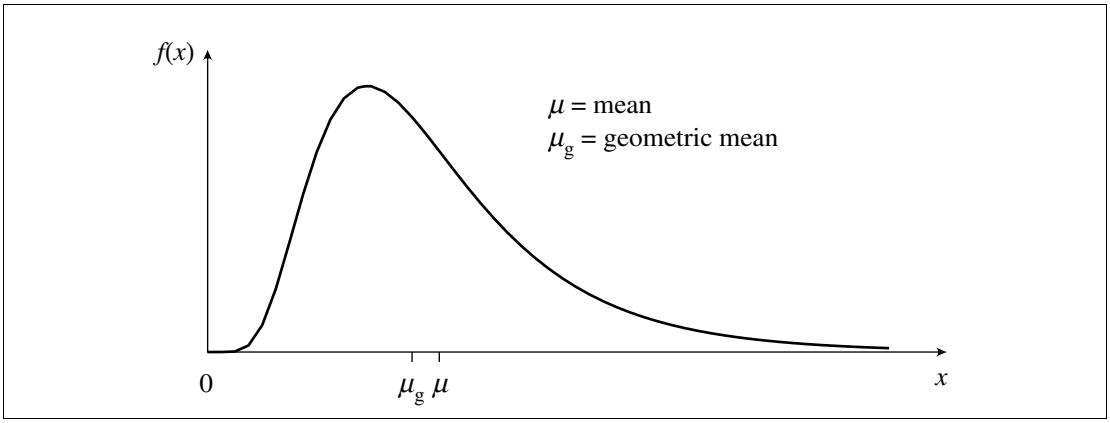

FIGURE 19.6 — A log-normal distribution

By definition, a quantity X has a log-normal (or lognormal) distribution if the logarithm of X is normally distributed. The product of a large number of independent positive random variables with similar variances is approximately log-normal, because the logarithm of the product is a sum of independent random variables, and the sum is approximately normal. The concentration of a contaminant in the environment tends to be log-normal because it is the result of processes of concentration and dilution, which are multiplicative.

The distribution of a log-normal quantity X can be uniquely specified by the mean $\mu_{\ln X}$ and variance $\sigma^2_{\ln X}$ of $\ln X$, but more commonly used parameters are the *geometric mean* $\mu_g = \exp(\mu_{\ln X})$ and the *geometric standard deviation* $\sigma_g = \exp(\sigma_{\ln X})$. The geometric mean and geometric standard deviation are defined so that, if k is a positive number, the probability that X will fall between μ_g / σ_g^k and $\mu_g \sigma_g^k$ is the same as the probability that $\ln X$, which is normally distributed, will fall between $\mu_{\ln X} - k\sigma_{\ln X}$ and $\mu_{\ln X} + k\sigma_{\ln X}$. For example, the value of X will be between μ_g / σ_g^2 and $\mu_g \sigma_g^2$ about 95 % of the time.

Although the mean and median of a normal distribution are identical, for a log-normal distribution these values are distinct. The median, in fact, is the same as the geometric mean μ_g. As shown in Figure 19.6, the mean μ is larger than the geometric mean μ_g . The mean may be cal-

culated from the geometric mean and geometric standard deviation as shown in Table G.6 in Appendix G.[18,19]

The log-normal distribution is important for the interpretation of environmental radiation data, but it may also have applications in the laboratory. Two possible applications are decay factors $e^{-\lambda t}$ based on uncertain time measurements and concentrations of contaminants in laboratory reagents.

19A.2.3 Chi-squared Distributions

If $Z_1, Z_2, \ldots, Z_\nu$ are independent random variables and each has the standard normal distribution, the sum $Z_1^2 + Z_2^2 + \cdots + Z_\nu^2$ has a *chi-squared* (or *chi-square*) *distribution with v degrees of freedom*. A chi-squared distribution, like a log-normal distribution, is asymmetric and does not include negative values. For large ν, the chi-squared distribution is approximately normal. Figure 19.7 shows the densities for chi-square distributions with 1, 2, 3 and 10 degrees of freedom.

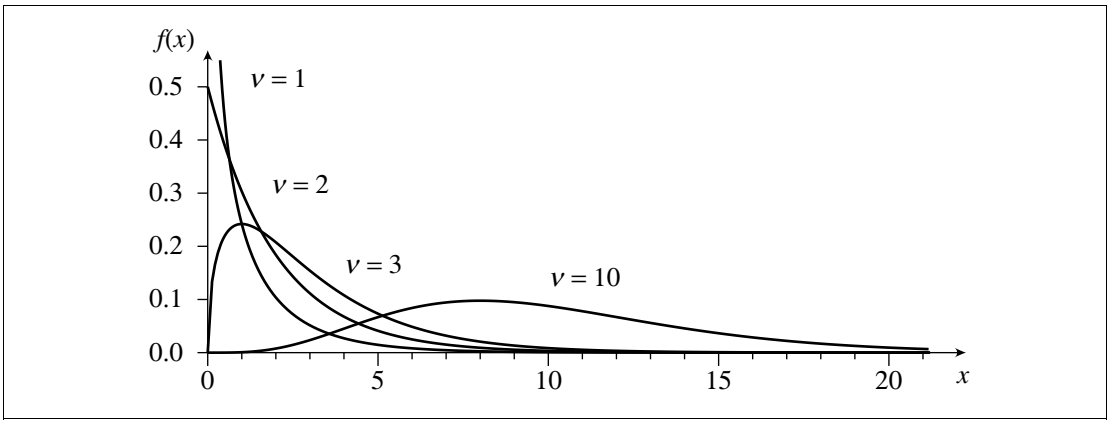

FIGURE 19.7 — Chi-squared distributions

Chi-squared distributions are used frequently in hypothesis testing, especially for tests of hypotheses about the variances of normally distributed data. Chi-squared distributions also appear in least-squares analysis (see Attachment 19C).

[18] Given the mean μ and standard deviation σ of the log-normal distribution, the geometric mean and geometric standard deviation may be calculated as $\mu_g = \mu^2 / \sqrt{\mu^2 + \sigma^2}$ and $\sigma_g = \exp\left(\sqrt{\ln(1 + \sigma^2 / \mu^2)}\right)$.

[19] Note that the symbols μ and σ are often used to denote the mean and standard deviation of ln X, which is normally distributed, rather than those of X, which is log-normally distributed.

A sum of independent chi-squared random variables is also chi-squared. Specifically, if X and Y are independent chi-squared random variables with ν_1 and ν_2 degrees of freedom, respectively, then $X + Y$ has a chi-squared distribution with $\nu_1 + \nu_2$ degrees of freedom.

The mean of a chi-squared distribution equals the number of degrees of freedom v, and the variance equals $2v$. The median does not have a simple formula.

19A.2.4 *T*-Distributions

If Z is standard normal, X is chi-squared with v degrees of freedom, and Z and X are independent, then $Z / \sqrt{X / v}$ has a *Student's t-distribution with v degrees of freedom*. A *t*-distribution is symmetric and mound-shaped like a normal distribution and includes both positive and negative values. Figure 19.8 shows the pdf for a *t*-distribution with 3 degrees of freedom. A dotted standard normal curve is also shown for comparison.

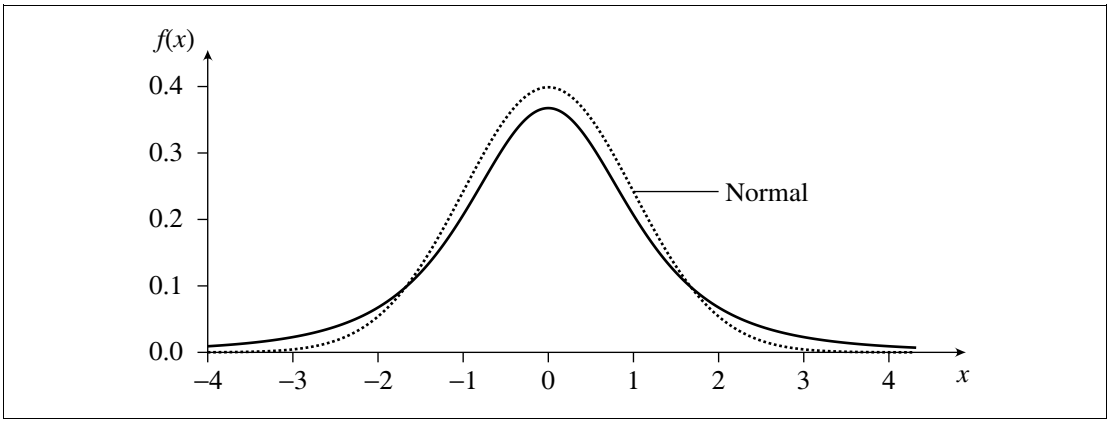

FIGURE 19.8 — The *t*-distribution with 3 degrees of freedom

When v is large, the *t*-distribution is virtually identical to the standard normal distribution.

The median of a *t*-distribution is zero. The mean is also zero if $v > 1$ but is undefined for $v = 1$. The variance equals $v / (v - 2)$ if $v > 2$ and is undefined otherwise.

T-distributions are often used in tests of hypotheses about the means of normally distributed data and are important in statistical quality control. *T*-distributions are also used in the procedure described in Attachment 19D for calculating measurement coverage factors.

If $X_1, X_2, \ldots, X_n$ are independent and normally distributed with the same mean μ and the same variance, then the quantity

$$\frac{\overline{X} - \mu}{s_X / \sqrt{n}}$$

where $\overline{X}$ is the arithmetic mean and s_X is the experimental standard deviation, has a *t*-distribution with $n - 1$ degrees of freedom.

If $X_1, X_2, \ldots, X_n, Y$ are independent and normally distributed with the same mean and variance, then the quantity

$$\frac{Y - \overline{X}}{s_X\sqrt{1 + 1/n}}$$

where $\overline{X}$ is the arithmetic mean of the X_i and s_X is the experimental standard deviation, has a *t*-distribution with $n - 1$ degrees of freedom.

If Z is standard normal, X is chi-squared with v degrees of freedom, Z and X are independent, and δ is a constant, then $(Z + \delta) / \sqrt{X / v}$ has the *noncentral t-distribution* with v degrees of freedom and noncentrality parameter δ (Stapleton, 1995). When the (central) *t*-distribution is used to test the null hypothesis that two normal distributions have the same mean, a noncentral *t*-distribution describes the distribution of the test statistic if the null hypothesis is false. For example, if $X_1, X_2, \ldots, X_n, Y$ are independent and normally distributed with the same variance σ^2, and $X_1, X_2, \ldots, X_n$ have the same mean μ_X, then the statistic

$$\frac{Y - \overline{X}}{s_X\sqrt{1 + 1/n}}$$

where $\overline{X}$ is the arithmetic mean of the X_i and s_X is the experimental standard deviation, has a *t*-distribution with $n - 1$ degrees of freedom if $\mu_X = \mu_Y$, but it has a noncentral *t*-distribution with noncentrality parameter

$$\delta = \frac{\mu_Y - \mu_X}{\sigma\sqrt{1 + 1/n}}$$

if $\mu_X \neq \mu_Y$.

The noncentral *t*-distribution is useful in the theory of detection limits and appears in Attachment 20A of Chapter 20, "Detection and Quantification Capabilities."

19A.2.5 Rectangular Distributions

If X only assumes values between a_- and a_+ and all such values are equally likely, the distribution of X is called a *rectangular distribution*, or a *uniform distribution* (see Figure 19.9).

The mean and median of the rectangular distribution equal the midrange $(a_- + a_+) / 2$, and the standard deviation is $(a_+ - a_-) / 2\sqrt{3}$.

Rectangular distributions are frequently used for Type B evaluations of standard uncertainty (see Sections 19.4.2.2 and 19.5.11).

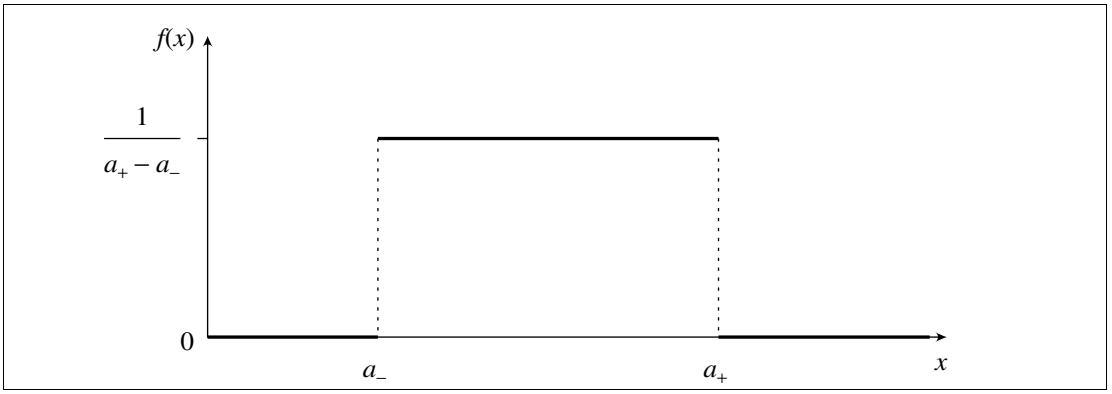

FIGURE 19.9 — A rectangular distribution

19A.2.6 Trapezoidal and Triangular Distributions

Another type of bounded distribution used for Type B evaluations of standard uncertainty is a *trapezoidal* distribution, which is described in Section 19.4.2.2. If X has a trapezoidal distribution, it only assumes values between two numbers a_- and a_+, but values near the midrange $(a_- + a_+) / 2$ are more likely than those near the extremes. The pdf for a symmetric trapezoidal distribution is shown in Figure 19.10. Asymmetric trapezoidal distributions are not considered here.

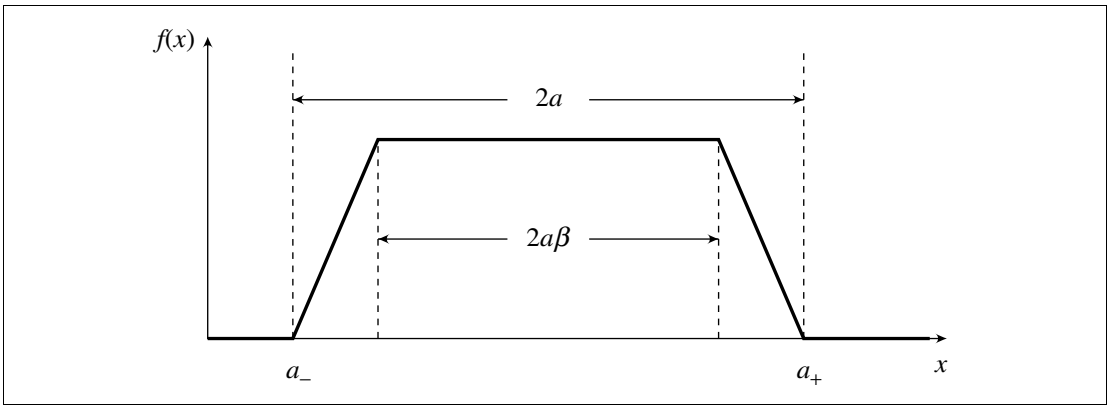

FIGURE 19.10 — A trapezoidal distribution

The mean and median of this distribution are both equal to the midrange. If the width of the trapezoid at its base is $2a$ and the width at the top is $2a\beta$, where $0 < \beta < 1$, then the standard deviation is $a\sqrt{(1 + \beta^2) / 6}$. As β approaches 0, the trapezoidal distribution approaches a *triangular distri-*

bution, whose standard deviation is $a / \sqrt{6}$, or $(a_+ - a_-) / 2\sqrt{6}$. As β approaches 1, the distribution approaches the rectangular distribution described in Section 19A.2.5.

19A.2.7 Exponential Distributions

The *exponential distribution* describes the life of an unstable atomic nucleus, whose remaining life does not depend on its current age. The distribution is described by one parameter, often denoted by λ, which represents the fractional decay rate. The mean of the distribution is $1 / \lambda$ and its variance is $1 / \lambda^2$. The median is the same as the half-life of the radionuclide. The pdf for an exponential distribution is shown in Figure 19.11.

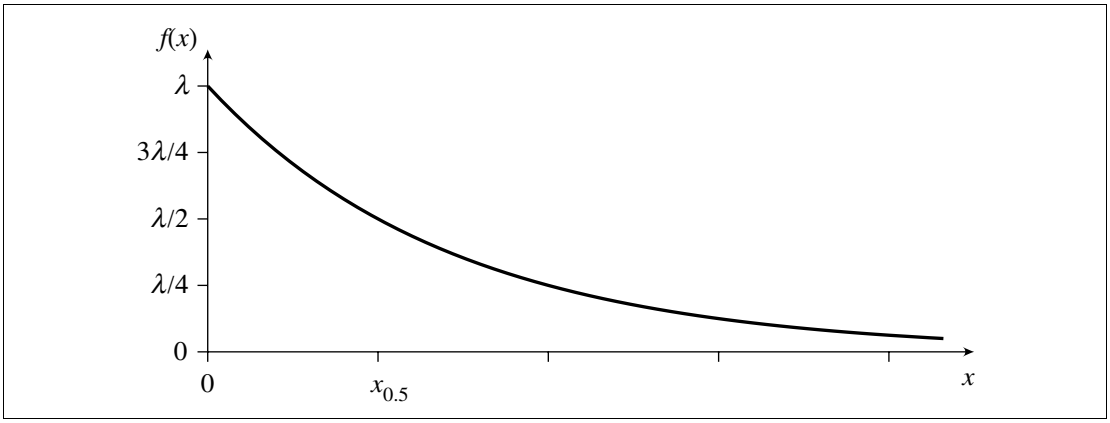

FIGURE 19.11 — An exponential distribution

The exponential distribution also describes waiting times between events in a Poisson process. For example, if the instrument background for a radiation counter follows the Poisson model with mean count rate r_B (see Section 19A.2.9), the waiting times between counts are exponentially distributed with parameter r_B.

19A.2.8 Binomial Distributions

The *binomial distribution*, introduced in Section 19.5.2, arises when one counts the outcomes of a series of n independent and identical experiments, each of which can produce the result "success" or "failure." If the probability of success for each event is p, the number of successes has a binomial distribution with parameters n and p. Important facts about the binomial distribution include the following:

- The distribution is discrete; its only possible values are 0, 1, 2, …, n.
- The mean of the distribution is np.
- The variance is $np(1 - p)$.
- If n is large and p is not close to 0 or 1, the distribution is approximated well by a normal distribution.

If X is binomial with parameters n and p, then for $k = 0, 1, 2, \ldots, n$, the probability that $X = k$ is given by the equation

$$\Pr[X = k] = \binom{n}{k} p^k (1-p)^{n-k} \tag{19.36}$$

where $\binom{n}{k}$ denotes a binomial coefficient, which equals $\frac{n!}{k!(n-k)!}$.

19A.2.9 Poisson Distributions

As explained in Section 19.5.2, the *Poisson distribution* arises naturally as an approximation to the binomial distribution when n is large and p is small. Even if n is not large, the variance of the binomial distribution can be approximated using the Poisson model if p is small. Other important facts about a Poisson distribution include the following:

- The distribution is discrete; its only possible values are the nonnegative integers 0, 1, 2, ….
- The mean and variance of the distribution are equal.
- If the mean is large, the distribution is well approximated by a normal distribution.
- A sum of independent Poisson random variables is also Poisson.

If X has a Poisson distribution with mean μ, then for any nonnegative integer n, the probability that $X = n$ is given by

$$\Pr[X = n] = \frac{\mu^n e^{-\mu}}{n!} \tag{19.37}$$

The Poisson distribution is related to the chi-squared distribution, since

$$\Pr[X \le n] = \Pr[\chi^2(2n + 2) \ge 2\mu] \qquad \text{and} \qquad \Pr[X \ge n] = \Pr[\chi^2(2n) \le 2\mu] \tag{19.38}$$

where $\chi^2(v)$ denotes a chi-squared random variable with v degrees of freedom. This fact allows one to use quantiles of a chi-squared distribution to construct a confidence interval for μ based on a single observation $X = n$ (Stapleton, 1995). Table 19.3 lists 95 % two-sided confidence intervals for μ some small values of n. For large values of n, the quantiles $\chi^2_p(2n)$ and $\chi^2_p(2n + 2)$ may be approximated using the Wilson-Hilferty formula (NBS, 1964):

$$\chi^2_p(v) \approx v\left(1 - \frac{2}{9v} + z_p\sqrt{\frac{2}{9v}}\right)^3 \tag{19.39}$$

As noted above, when the mean μ is large, the Poisson distribution may be approximated by a normal distribution. Specifically,

$$\Pr[X \le n] \approx \Phi\left(\frac{n + 0.5 - \mu}{\sqrt{\mu}}\right) \tag{19.40}$$

where Φ denotes the distribution function of the standard normal distribution. For most purposes, this approximation is adequate if $\mu \ge 20$.

Figures 19.12a and b show how the normal approximation improves as μ increases from 3 to 100. For any n, the probability $\Pr[X \le n]$ is represented by the total area of bars 0 to n, while the value given by the normal approximation is represented by the total area under the dotted curve to the left of the vertical line at $n + 0.5$.

TABLE 19.3 — 95 % confidence interval for a Poisson mean

n	$\mu_{lower} = \frac{1}{2}\chi^2_{0.025}(2n)$	$\mu_{upper} = \frac{1}{2}\chi^2_{0.975}(2n+2)$
0	0.000	3.689
1	0.025	5.572
2	0.242	7.225
3	0.619	8.767
4	1.090	10.242
5	1.623	11.668

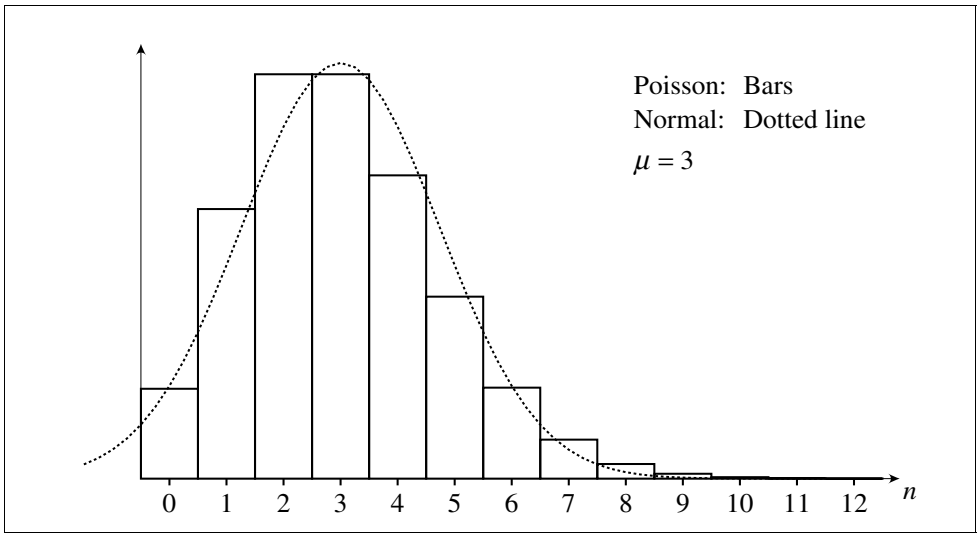

FIGURE 19.12a — Poisson distribution vs. normal distribution, $\mu = 3$

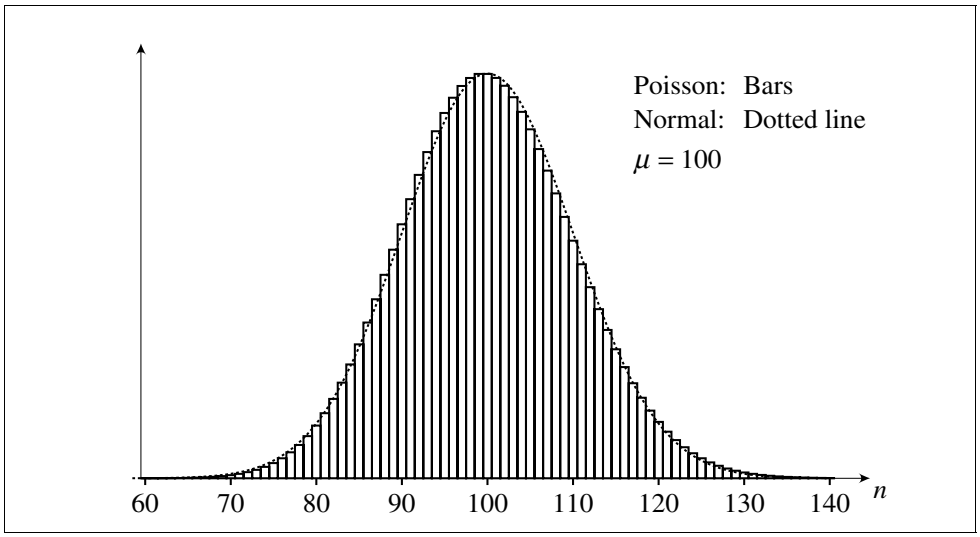

FIGURE 19.12b — Poisson distribution vs. normal distribution, $\mu = 100$

19A.3 References

National Bureau of Standards (NBS). 1964. *Handbook of Mathematical Functions*. Applied Mathematics Series 55, National Bureau of Standards, Gaithersburg, MD.

Stapleton, James H. 1995. *Linear Statistical Models*. John Wiley and Sons, New York, NY.

ATTACHMENT 19B
Example Calculations

19B.1 Overview

The following example shows how to calculate the combined standard uncertainty for a typical radioanalytical measurement.

19B.2 Sample Collection and Analysis

A soil sample is analyzed for $^{239/240}$Pu and ^{238}Pu by alpha-particle spectrometry.

- The sample is collected on July 10, 1999, at 11:17 am EDT, and shipped to a laboratory for analysis.

- The entire laboratory sample is dried, weighed and ground to a maximum particle size of 1.0 mm. The dry weight is approximately 2 kg.

- The prepared sample is homogenized, and a test portion is removed by increments. The documented procedure requires a test portion of approximately 0.5 g.

- The test portion is weighed and the mass is found to be 0.5017 g. The standard uncertainty of the mass includes contributions from repeatability, linearity, and sensitivity drift.

- A 1-milliliter aliquant of ^{242}Pu tracer is added to the test portion. The activity concentration of the tracer solution has previously been measured as 0.0705 Bq/mL with a standard uncertainty of 0.0020 Bq/mL on June 30, 1999, at 11:00 am CDT. The aliquant is dispensed by a pipet, whose dispensed volume has a combined standard uncertainty previously determined to be 0.0057 mL.

- After fusion, dissolution, chemical purification, and coprecipitation, a test source on a stainless steel planchet is prepared for counting in an alpha-particle spectrometer.

- The efficiency of the spectrometer for the chosen geometry, which is assumed to be independent of the particle energy, has previously been measured as 0.2805 with a standard uncertainty of 0.0045.

- A blank source is counted in the spectrometer for 60,000 s. The blank consists of a filter mounted on a planchet in the same geometry as the test source. In the ^{242}Pu region of interest, 2 counts are measured; and in the ^{238}Pu region of interest, 0 counts are measured. Historical

data for this and similar spectrometers at the laboratory indicate that the background is stable between measurements.

- The test source is placed in the spectrometer and counted for 60,000 s, beginning on August 24, 1999, at 4:47 pm CDT. In the ^{242}Pu region of interest, 967 counts are measured; and in the ^{238}Pu region of interest, 75 counts are measured.

- It is assumed that there is no detectable plutonium in the reagents; however, a method blank is analyzed simultaneously using a different spectrometer to check for contamination of reagents and glassware.

In this example the measurand will be the specific activity of ^{238}Pu in the 2-kilogram sample (dry weight) at the time of collection.

19B.3 The Measurement Model

The following notation will be used:

m_S	is the mass of the test portion (0.5017 g)
m_L	is the mass of the entire laboratory sample (~2000 g)
d	is the mesh size of the sieve (1.0 mm)
c_T	is the tracer activity concentration (0.0705 Bq/mL)
V_T	is the tracer aliquant volume (1 mL)
t_B	is the blank count time (60,000 s)
t_S	is the count time for the test source (60,000 s)
N_S	is the total count in a region of interest when the source is counted (^{238}Pu or ^{242}Pu)
N_B	is the count in a region of interest when the blank is counted (^{238}Pu or ^{242}Pu)
R	is the fraction of alpha particles with measured energy in the region of interest (^{238}Pu or ^{242}Pu)
D	is the decay-correction factor (^{238}Pu or ^{242}Pu)
ε	is the alpha-particle counting efficiency
Y	is the plutonium chemical yield fraction
F_S	is the subsampling factor (estimated as 1.00)
a_{238}	is the specific activity of ^{238}Pu in the dried laboratory sample, decay-corrected to the time of collection

Subscripts will be used to distinguish between quantities associated with particular regions of interest (^{238}Pu or ^{242}Pu).

The decay-correction factor for either isotope is calculated as follows:

$$D = \mathrm{e}^{-\lambda t_\mathrm{D}} \frac{1 - \mathrm{e}^{-\lambda t_\mathrm{S}}}{\lambda t_\mathrm{S}}$$

where λ is the decay constant (s^{-1}) and t_D is the time between collection and the start of the counting measurement (3,911,400 s). Since λt_S is small for both isotopes in this example, D may be approximated accurately by

$$D = \mathrm{e}^{-\lambda (t_\mathrm{D} + t_\mathrm{S}/2)}$$

The half-lives of ^{238}Pu and ^{242}Pu are 87.75 a and 375,800 a, respectively. So,

$$D_{238} = \exp\left(\frac{-\ln 2}{(87.75\ \mathrm{a}) \times (365.2422\ \mathrm{d/a}) \times (86{,}400\ \mathrm{s/d})} \left(3{,}911{,}400\ \mathrm{s} + \frac{60{,}000\ \mathrm{s}}{2} \right) \right)$$
$$= 0.9990$$

and $D_{242} = 1.000$.

Dead time is negligible in this example; so, no distinction is made between the real time and the live time. If the real time were greater than the live time, the correction for decay during the counting period would be based on the real time.

The fraction of alpha particles of each isotope actually measured in the nominal region of interest is estimated to lie between 0.96 and 1.00. A rectangular distribution is assumed, with center at 0.98 and half-width equal to 0.02. Then the Type B standard uncertainties of R_{238} and R_{242} are

$$u(R_{238}) = u(R_{242}) = \frac{0.02}{\sqrt{3}} = 0.01155$$

The chemical yield of plutonium is calculated using the model

$$Y = \frac{N_{\mathrm{S},242} / t_\mathrm{S} - N_{\mathrm{B},242} / t_\mathrm{B}}{c_\mathrm{T} V_\mathrm{T} \varepsilon R_{242} D_{242}}$$

Then the following model is used to estimate the measurand.

$$a_{238} = \frac{N_{\mathrm{S},238} / t_\mathrm{S} - N_{\mathrm{B},238} / t_\mathrm{B}}{m_\mathrm{S} Y \varepsilon R_{238} D_{238} F_\mathrm{S}}$$

When values are inserted,

$$Y = \frac{967 / (60{,}000 \text{ s}) - 2 / (60{,}000 \text{ s})}{(0.0705 \text{ Bq/mL}) \times (1 \text{ mL}) \times 0.2805 \times 0.98 \times 1} = 0.82990$$

$$a_{238} = \frac{75 / (60{,}000 \text{ s}) - 0 / (60{,}000 \text{ s})}{(0.5017 \text{ g}) \times 0.82990 \times 0.2805 \times 0.98 \times 0.9990 \times 1.00} = 0.010932 \text{ Bq/g}$$

(or 10.932 Bq/kg)

19B.4 The Combined Standard Uncertainty

The efficiency, ε, effectively cancels out of the equation for a_{238}, because it is multiplied by the yield Y and also appears as a factor in the denominator of the expression for Y (see also Section 19.5.6). Therefore, the uncertainty of ε has no effect on the uncertainty of a_{238}. When using the uncertainty propagation formula to calculate the combined standard uncertainty of a_{238}, one might include a covariance term for $u(Y, \varepsilon)$ to account for the relationship between the measured values of Y and ε, but it is simpler to treat $Y\varepsilon$ as one variable. Application of the first-order uncertainty propagation formula (Section 19.4.3) to the equations above then gives the following:

$$u_c^2(Y\varepsilon) = \frac{u^2(N_{S,242}) / t_S^2 + u^2(N_{B,242}) / t_B^2}{c_T^2 V_T^2 R_{242}^2 D_{242}^2} + (Y\varepsilon)^2 \left(\frac{u^2(c_T)}{c_T^2} + \frac{u^2(V_T)}{V_T^2} + \frac{u^2(R_{242})}{R_{242}^2} \right)$$

$$u_c^2(a_{238}) = \frac{u^2(N_{S,238}) / t_S^2 + u^2(N_{B,238}) / t_B^2}{m_S^2 (Y\varepsilon)^2 R_{238}^2 D_{238}^2} + a_{238}^2 \left(\frac{u^2(m_S)}{m_S^2} + \frac{u^2(Y\varepsilon)}{(Y\varepsilon)^2} + \frac{u^2(R_{238})}{R_{238}^2} + \frac{u^2(F_S)}{F_S^2} \right)$$

All other input estimates are assumed to be uncorrelated.

Note that $u^2(F_S)$ is the subsampling variance associated with taking a small test portion (0.5017 g) from a much larger sample (2000 g). The estimation method suggested in Section 19.5.12 will be used here to evaluate $u(F_S)$.

$$u(F_S) = \sqrt{\left(\frac{1}{m_S} - \frac{1}{m_L} \right) k d^3} \qquad \text{where } k = 0.0004 \text{ g/mm}^3$$

$$= \sqrt{\left(\frac{1}{0.5017 \text{ g}} - \frac{1}{2000 \text{ g}} \right) (0.0004 \text{ g/mm}^3)(1.0 \text{ mm})^3}$$

$$= 0.0282 .$$

Appendix F provides more information about subsampling errors and methods for estimating their variances.

The standard uncertainty of the mass of the test portion, m_S, is evaluated using the methods described in Section 19.5.9. The total uncertainty of m_S has components due to repeatability, linearity, and sensitivity drift (environmental factors). Assume the repeatability standard deviation is 0.0001 g, the linearity tolerance is 0.0002 g, and the relative standard uncertainty due to sensitivity drift is 1×10^{-5}. If the balance is zeroed with an empty container on the pan, the soil is added to the container, and the display is read, then the standard uncertainty of the mass m_S is

$$u(m_S) = \sqrt{(0.0001\ \text{g})^2 + (0.0002\ \text{g})^2 + (0.5017\ \text{g})^2(1 \times 10^{-5})^2} = 2.2 \times 10^{-4}\ \text{g}$$

Since extremely low counts are possible, each Poisson counting variance in this example will be estimated by the number of observed counts plus one (see Section 19.5.2.2 and Section 19D.3 of Attachment 19D). So, for example, $u(N_{B,238})$ equals one, not zero.

Table 19.4 summarizes the input estimates and their standard uncertainties.

TABLE 19.4 — Input estimates and standard uncertainties

INPUT QUANTITY	INPUT ESTIMATE	STANDARD UNCERTAINTY	MEASUREMENT UNIT	TYPE OF EVALUATION
m_S	0.5017	2.2×10^{-4}	g	Combined*
c_T	0.0705	0.0020	Bq/mL	Combined*
V_T	1.0000	0.0057	mL	Combined*
t_B	60,000	Negligible	s	B
t_S	60,000	Negligible	s	B
$N_{B,238}$	0	1	counts	B
$N_{B,242}$	2	1.73	counts	B
$N_{S,238}$	75	8.72	counts	B
$N_{S,242}$	967	31.1	counts	B
R_{238}, R_{242}	0.98	0.01155	none	B
ε	0.2805	0.0045	none	Combined*
F_S	1.00	0.0282	none	B
D_{238}	0.9990	Negligible	none	B
D_{242}	1.0000	Negligible	none	B

* "Combined" here means "determined by uncertainty propagation."

Other possible sources of uncertainty in alpha-particle spectrometry measurements include:

- uncertainties in half-lives and decay times;
- spillover and baseline interferences caused by poor peak resolution;
- incomplete equilibration of tracer and analyte before chemical separation; and
- changing instrument background.

These uncertainties are evaluated as negligible in this example. Uncertainties associated with half-lives and decay times are negligible, because the decay times in the example are much shorter than the half-lives; but in practice one should confirm that any other uncertainties are small enough to be neglected.

When values are inserted into the formulas

$$u_c^2(Y\varepsilon) = \frac{968 / (60{,}000\ \text{s})^2 + 3 / (60{,}000\ \text{s})^2}{(0.0705\ \text{Bq/mL})^2 \times (1\ \text{mL})^2 \times 0.98^2 \times 1^2} + (0.82990 \times 0.2805)^2 \left(\frac{0.0020^2}{0.0705^2} + \frac{0.0057^2}{1^2} + \frac{0.01155^2}{0.98^2} \right)$$

$$= 0.0001094007$$

$$= 0.01046^2$$

and

$$u_c^2(a_{238}) = \frac{76 / (60{,}000\ \text{s})^2 + 1 / (60{,}000\ \text{s})^2}{(0.5017\ \text{g})^2 \times (0.82990 \times 0.2805)^2 \times 0.98^2 \times 0.9990^2} + (0.010932\ \text{Bq/g})^2 \left(\frac{(2.2 \times 10^{-4})^2}{0.5017^2} + \frac{0.01046^2}{(0.82990 \times 0.2805)^2} + \frac{0.01155^2}{0.98^2} + \frac{0.0282^2}{1^2} \right)$$

$$= 1.98915 \times 10^{-6}\ \text{Bq}^2/\text{g}^2$$

$$= (0.001410\ \text{Bq/g})^2$$

So, $u_c(a_{238}) = 0.00141\ \text{Bq/g}$ or $1.41\ \text{Bq/kg}$. If the result is to be reported with an expanded uncertainty calculated from the combined standard uncertainty $u_c(a_{238})$ and a coverage factor $k = 2$, the result should appear as $(0.0109 \pm 0.0028)\ \text{Bq/g}$ or $(10.9 \pm 2.8)\ \text{Bq/kg}$ (dry weight).

ATTACHMENT 19C
Multicomponent Measurement Models

19C.1 Introduction

In this attachment, the term "multicomponent measurement model" means a mathematical model with more than one output quantity calculated from the same set of input quantities. One common application of a multicomponent model is the determination of a calibration curve involving two or more parameters. In principle, the approach to uncertainty propagation described in Section 19.4 applies equally well to single-component or multicomponent models. However, a straightforward implementation of the uncertainty propagation formula for some multicomponent models may be tedious unless software for automatic uncertainty propagation is available.

At the time of this writing, the joint working group responsible for the *GUM* is reported to be developing additional guidance to deal with multicomponent models, but the guidance is not yet available.

19C.2 The Covariance Matrix

A multicomponent model is most naturally described in terms of vectors and matrices, and the remainder of this attachment assumes the reader is familiar with those concepts and with the notation commonly used to describe them. The single-component model, $Y = f(X_1, X_2, \ldots, X_N)$, which was used earlier, is now replaced by a multicomponent model, $\boldsymbol{Y} = \boldsymbol{f}(\boldsymbol{X})$, where $\boldsymbol{X}$ and $\boldsymbol{Y}$ denote column vectors and $\boldsymbol{f}$ denotes a vector-valued function of $\boldsymbol{X}$. The input vector, which is formed from the input estimates, x_j, will be denoted by $\boldsymbol{x}$, and the output vector, which is formed from the output estimates, y_i, will be denoted by $\boldsymbol{y}$. The estimated variances and covariances of all the input estimates are arranged in a square matrix, called the *covariance matrix* and denoted here by $\boldsymbol{u}^2(\boldsymbol{x})$, whose ij^{th} element equals the covariance $u(x_i, x_j)$. Application of the covariance equation in Section 19.4.4 leads to the following expression for the covariance matrix of the output vector, $\boldsymbol{y}$.

$$\boldsymbol{u}^2(\boldsymbol{y}) = \left(\frac{\partial \boldsymbol{f}}{\partial \boldsymbol{x}} \right) \boldsymbol{u}^2(\boldsymbol{x}) \left(\frac{\partial \boldsymbol{f}}{\partial \boldsymbol{x}} \right)' \tag{19.46}$$

In this equation, $\partial \boldsymbol{f} / \partial \boldsymbol{x}$ denotes the matrix whose ij^{th} element is $\partial f_i / \partial x_j$.

19C.3 Least-Squares Regression

One application for which specialized multicomponent methods for uncertainty propagation may be useful is least-squares regression. For example the method of least squares may be used to find an approximate solution, $\hat{\boldsymbol{y}}$, of a matrix equation of the form

$$\boldsymbol{A}\boldsymbol{y} \cong \boldsymbol{b} \tag{19.47}$$

where the components of the vector $\boldsymbol{b}$ have uncertainties. The least-squares solution for this problem can usually be expressed as

$$\hat{\boldsymbol{y}} = (\boldsymbol{A}'\boldsymbol{W}\boldsymbol{A})^{-1}\boldsymbol{A}'\boldsymbol{W}\boldsymbol{b} \tag{19.48}$$

where $\boldsymbol{W}$ denotes a diagonal weight matrix, whose i^{th} diagonal element is the inverse of the variance of b_i. If there is no uncertainty in the matrix $\boldsymbol{A}$, and the elements of $\boldsymbol{b}$ are uncorrelated, then the covariance matrix for $\hat{\boldsymbol{y}}$ is given simply by

$$\boldsymbol{u}^2(\hat{\boldsymbol{y}}) = (\boldsymbol{A}'\boldsymbol{W}\boldsymbol{A})^{-1} \tag{19.49}$$

If there are uncertainties in the elements of $\boldsymbol{A}$, the expression above is incomplete. Suppose the elements of $\boldsymbol{A}$ are functions of variables $z_1, z_2, \ldots, z_r$, whose estimated variances and covariances are available. Arrange these variables, z_j, in a column vector, $\boldsymbol{z}$, and let $\boldsymbol{u}^2(\boldsymbol{z})$ denote the covariance matrix. If the b_i are not correlated with the z_j, then a more complete expression for the covariance matrix of $\hat{\boldsymbol{y}}$ is the following.

$$\boldsymbol{u}^2(\hat{\boldsymbol{y}}) = (\boldsymbol{A}'\boldsymbol{W}\boldsymbol{A})^{-1} + \left(\frac{\partial \hat{\boldsymbol{y}}}{\partial \boldsymbol{z}}\right) \boldsymbol{u}^2(\boldsymbol{z}) \left(\frac{\partial \hat{\boldsymbol{y}}}{\partial \boldsymbol{z}}\right)' \tag{19.50}$$

The derivative matrix, $\partial\hat{\boldsymbol{y}} / \partial\boldsymbol{z}$, which appears above, may be calculated column by column. The j^{th} column of $\partial\hat{\boldsymbol{y}} / \partial\boldsymbol{z}$ is given by the formula

$$\frac{\partial \hat{\boldsymbol{y}}}{\partial z_j} = (\boldsymbol{A}'\boldsymbol{W}\boldsymbol{A})^{-1}\left(\frac{\partial \boldsymbol{A}'}{\partial z_j}\boldsymbol{W}(\boldsymbol{b} - \boldsymbol{A}\hat{\boldsymbol{y}}) - \boldsymbol{A}'\boldsymbol{W}\frac{\partial \boldsymbol{A}}{\partial z_j}\hat{\boldsymbol{y}}\right) \tag{19.51}$$

where $\partial\boldsymbol{A} / \partial z_j$ denotes the matrix obtained from $\boldsymbol{A}$ by differentiating each element with respect to z_j. If the uncertainties in the matrix $\boldsymbol{A}$ are large, even this method of uncertainty propagation may be inadequate (e.g., see Fuller, 1987).

19C.4 References

Fuller, Wayne A. 1987. *Measurement Error Models*. John Wiley and Sons, New York, NY.

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

ATTACHMENT 19D
Estimation of Coverage Factors

19D.1 Introduction

Although it is common for laboratories to use a fixed coverage factor such as 2 or 3 when determining an expanded uncertainty for a measured value, the true coverage probability for the resulting interval may be lower than expected if the standard uncertainties of the input estimates are determined from evaluations with too few degrees of freedom. This attachment summarizes a general method presented in Annex G of the *GUM* for determining appropriate coverage factors in these circumstances (ISO, 1995). Section 19D.3 applies the method to Poisson counting uncertainties.

19D.2 Procedure

19D.2.1 Basis of Procedure

When one evaluates a parameter, θ, statistically by making a series of n independent, unbiased measurements under the same measurement conditions and averaging the results, x_i, if the results are approximately normally distributed, a confidence interval for θ may be constructed using the fact that the quantity $(\bar{x} - \theta) / s(\bar{x})$ has a t-distribution with $\nu = n - 1$ degrees of freedom. If the desired confidence level is p, then the confidence interval is $\bar{x} \pm t\,s(\bar{x})$, where $t = t_{(1+p)/2}(\nu)$ is the $(1 + p) / 2$-quantile of a t-distribution with ν degrees of freedom. Here, $\bar{x}$ is the result of the measurement of θ, and $s(\bar{x})$ is its standard uncertainty (Type A). The quantile, t, is the coverage factor that makes the coverage probability equal to p. For smaller values of ν, larger values of t are necessary to give the same coverage probability, because of the increased variability of the variance estimator, $s^2(\bar{x})$.

The procedure described below is derived by assuming that the output estimate, y, for a more complex measurement and the combined standard uncertainty, $u_c(y)$, can take the place of $\bar{x}$ and $s(\bar{x})$, respectively, in the confidence interval above; and that the appropriate coverage factor, k_p, can be approximated by a quantile of a t-distribution with an appropriate number of degrees of freedom. The number of degrees of freedom is determined from the estimated coefficient of variation of the variance estimator, $u_c^2(y)$.

19D.2.2 Assumptions

Assume the mathematical model for a measurement is $Y = f(X_1, X_2, \ldots, X_N)$, the input estimates $x_1, x_2, \ldots, x_N$ are independent, and the output estimate is $y = f(x_1, x_2, \ldots, x_N)$. Also assume that the combined standard uncertainty of y is not dominated by one component determined from a Type A evaluation with only a few degrees of freedom or from a Type B evaluation based on a distri-

bution very different from a normal distribution. Then the distribution of the output estimate y should be approximately normal, and the following procedure may be used to obtain a coverage factor, k_p, for the expanded uncertainty of y that gives a desired coverage probability, p.

19D.2.3 Effective Degrees of Freedom

First compute the *effective degrees of freedom* of the measurement, ν_{eff}, using the *Welch-Satterthwaite* formula

$$\frac{u_c^4(y)}{\nu_{\text{eff}}} = \sum_{i=1}^{N} \frac{u_i^4(y)}{\nu_i} \qquad \text{or} \qquad \nu_{\text{eff}} = \frac{u_c^4(y)}{\sum_{i=1}^{N} \frac{u_i^4(y)}{\nu_i}} \tag{19.52}$$

Here $u_i(y) = |\partial f / \partial x_i|\, u(x_i)$ is the component of the combined standard uncertainty generated by $u(x_i)$. If $u(x_i)$ is evaluated by a Type A method, then ν_i is the number of degrees of freedom for that evaluation. If $u(x_i)$ is evaluated instead by a Type B method, then ν_i may be defined as

$$\nu_i = \frac{1}{2}\frac{u^2(x_i)}{\sigma^2(u(x_i))} = \frac{1}{2}\left(\frac{\Delta u(x_i)}{u(x_i)}\right)^{-2} \tag{19.53}$$

where $\Delta u(x_i)$ is the estimated standard deviation of the standard uncertainty, $u(x_i)$, and $\sigma^2(u(x_i))$ denotes its square. This definition of ν_i for a Type B evaluation is an approximation based on the relationship between the number of degrees of freedom for a Type A evaluation and the coefficient of variation of the uncertainty estimator. In most cases estimation of $\Delta u(x_i)$ is subjective and requires professional judgment.[20]

In some cases one may consider the value of $\Delta u(x_i)$ for a Type B standard uncertainty to be zero or negligible, as for example when evaluating the uncertainty associated with rounding a number (Section 19.5.11) or when the standard uncertainty estimate, $u(x_i)$, is very conservative. In such cases one may assume $\nu_i = \infty$; so, the i^{th} term of the sum appearing in the denominator of the Welch-Satterthwaite formula vanishes.

If an input estimate, x_i, and its standard uncertainty, $u(x_i)$, are taken from a calibration certificate, the effective degrees of freedom for $u(x_i)$ may be stated on the certificate. In this case the stated number of degrees of freedom should be used as ν_i.

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[20] A more rigorously derived mathematical definition of ν_i in terms of $\Delta u(x_i)$ exists, but its use is not warranted given the usually subjective nature of the estimate of $\Delta u(x_i)$ and the other approximations involved in the Welch-Satterthwaite formula.

The number of effective degrees of freedom, ν_{eff}, satisfies the following inequalities.

$$\min_{1 \le i \le n} \nu_i \le \nu_{\text{eff}} \le \sum_{i=1}^{n} \nu_i \tag{19.54}$$

So, ν_{eff} is no worse than the worst value of ν_i and no better than the sum of all the ν_i. The maximum (best) value for ν_{eff} in Equation 19.54 is attained only if each ν_i is proportional to $u_i^2(y)$. This fact suggests that, at least for Type A uncertainty components, the fraction of the total uncertainty evaluation effort spent on a particular component, $u_i(y)$, should be based on the anticipated magnitude of $u_i^2(y)$.

19D.2.4 Coverage Factor

The coverage factor, k_p, is defined to be the $(1 + p) / 2$-quantile, $t_{(1+p)/2}(\nu_{\text{eff}})$, of a t-distribution with ν_{eff} degrees of freedom.[21] Since the calculated value of ν_{eff} will generally not be an integer, it must be truncated to an integer, or else an interpolated t-factor should be used. That is, if $n < \nu_{\text{eff}} < n + 1$, then use either $k_p = t_{(1+p)/2}(\lfloor \nu_{\text{eff}} \rfloor)$, where $\lfloor \cdot \rfloor$ denotes the truncation operator, or

$$k_p = (n + 1 - \nu_{\text{eff}})\, t_{(1+p)/2}(n) + (\nu_{\text{eff}} - n)\, t_{(1+p)/2}(n + 1) \tag{19.55}$$

The expanded uncertainty $U_p = k_p u_c(y)$ is estimated to have a coverage probability approximately equal to p.

EXAMPLE 19.31

Problem: Refer to the efficiency-calibration problem presented in Example 19.20 in Section 19.5.6. The efficiency for a radiation counter, ε, is calculated using the equation

$$\varepsilon = \frac{\overline{R}}{a_S}$$

where $\overline{R}$ (62.1854 $s^{-1} \cdot g^{-1}$) and its uncertainty (0.2301 $s^{-1} \cdot g^{-1}$) are determined from 15 replicate measurements (14 degrees of freedom), and a_S (150.0 Bq/g) and its uncertainty (2.0 Bq/g) are obtained from a calibration certificate. The calculated efficiency is 0.4146 and its combined standard uncertainty is 0.005736.

[21] The *GUM* uses the notation $t_p(\nu)$ to denote the $(1 + p) / 2$-quantile of a t-distribution with ν degrees of freedom (ISO, 1995), but the same notation in most statistical literature denotes the p-quantile (e.g., ISO, 1993). MARLAP follows the latter convention.

Assume the certificate states that the number of effective degrees of freedom for $u(a_S)$ is 12.5. Find the effective degrees of freedom for $u_c(\varepsilon)$, the coverage factor, $k_{0.95}$, that gives 95 % coverage probability, and the expanded uncertainty, $U_{0.95}$.

Solution: The component of the combined standard uncertainty of ε generated by $u(\overline{R})$ is

$$u_{\overline{R}}(\varepsilon) = \left|\frac{\partial \varepsilon}{\partial \overline{R}}\right| u(\overline{R}) = \frac{1}{a_S}\, u(\overline{R}) = \frac{0.2301\ \mathrm{s^{-1}\cdot g^{-1}}}{150.0\ \mathrm{Bq/g}} = 0.001534.$$

The component generated by $u(a_S)$ is

$$u_{a_S}(\varepsilon) = \left|\frac{\partial \varepsilon}{\partial a_S}\right| u(a_S) = \frac{|\overline{R}|}{a_S^2}\, u(a_S) = \frac{62.1854\ \mathrm{s^{-1}\cdot g^{-1}}}{(150.0\ \mathrm{Bq/g})^2}\,(2.0\ \mathrm{Bq/g}) = 0.0055276.$$

So, the number of effective degrees of freedom, v_{eff}, for $u_c(\varepsilon)$ is given by

$$v_{\mathrm{eff}} = \frac{u_c^4(\varepsilon)}{\dfrac{u_{\overline{R}}^4(\varepsilon)}{v_{\overline{R}}} + \dfrac{u_{a_S}^4(\varepsilon)}{v_{a_S}}} = \frac{(0.005736)^4}{\dfrac{0.001534^4}{15-1} + \dfrac{0.0055276^4}{12.5}} \approx 14.42.$$

Since 14.42 is not an integer, an interpolated *t*-factor may be used (see Table G.2 in Appendix G). The coverage factor for 95 % coverage probability is

$$k_{0.95} = (15 - 14.42)\,t_{0.975}(14) + (14.42 - 14)\,t_{0.95}(15) = (0.58)(2.145) + (0.42)(2.131) = 2.139.$$

So, the expanded uncertainty is

$$U_{0.95} = k_{0.95}\,u_c(\varepsilon) = (2.139)(0.005736) \approx 0.012.$$

19D.3 Poisson Counting Uncertainty

As stated in Section 19.5.2.2, the standard uncertainty in the number of counts, N, observed during a radiation measurement may often be estimated by $u(N) = \sqrt{N}$, according to the Poisson counting model. This method of evaluating the standard uncertainty is a Type B method; so, the effective degrees of freedom v for the evaluation should be determined from $\Delta u(N)$. The standard

deviation of $\sqrt{N}$ is always less than 0.65.[22] If N is greater than about 10, the standard deviation of $\sqrt{N}$ is approximately equal to 0.5, and, in this case, Equation 19.53 gives the estimate $v \approx 2N$. For smaller values of N, the same approximation is inadequate.

MARLAP recommends that the standard uncertainty, $u(N)$, and degrees of freedom, v, for a Poisson measured value, N, be estimated by

$$u(N) = \sqrt{N} \qquad \text{and} \qquad v = 2N \tag{19.56}$$

or, if very low counts are possible, by

$$u(N) = \sqrt{N + 1} \qquad \text{and} \qquad v = 2(N + 1) \tag{19.57}$$

If the expected count is greater than about 10, these formulas tend to give a coverage probability near the desired probability, p. When the expected count is small, the coverage probability tends to be greater than p.

Although the estimate $u(N) = \sqrt{N + 1}$ may be derived by the Bayesian approach to counting statistics assuming a flat prior distribution for the mean count (Friedlander et al., 1981), the recommended expressions for $u(N)$ and v in Equation 19.57 have been chosen for the purely practical reason that they are simple and seem to give satisfactory results. When the count is low, the assumptions underlying the Welch-Satterthwaite formula are usually violated, because the combined standard uncertainty is dominated by counting uncertainty, and the distribution of the count is not normal. However, even in this case, if the formula is used, the recommended expressions for $u(N)$ and v tend to give conservative results.

EXAMPLE 19.32

Problem: An alpha spectrometer is used to make a 60,000-second blank measurement followed by a 60,000-second sample measurement. The observed blank count is 2 and the observed sample count is 0. The net count rate is modeled as

[22] Taking the square root of a Poisson random variable is a common *variance-stabilizing transformation*, as described in Chapter 20 of *Experimental Statistics* (NBS, 1963). The stated (slightly conservative) upper bound for the standard deviation of $\sqrt{N}$ is based on calculations performed at the EPA's National Air and Radiation Environmental Laboratory, although the same approximate value may be determined by inspecting Figure 20-2 of NBS (1963). The precise calculation maximizes a function $f(x)$ whose value is the variance of the square root of a Poisson random variable with mean x. The first derivative of f is positive, decreasing and convex between $x = 0$ and the location of the maximum of the function at $x = 1.31895$; so, Newton's Method converges to the solution from below. The maximum value of f is found to be $(0.642256)^2$.

$$R_N = \frac{N_S}{t_S} - \frac{N_B}{t_B}$$

where

R_N is the net count rate (-3.333×10^{-5} s^{-1});
N_S is the sample count (0);
t_S is the sample count time (60,000 s);
N_B is the blank count (2); and
t_B is the blank count time (60,000 s).

Assume the only source of uncertainty is Poisson counting statistics. Determine the effective degrees of freedom for $u_c(R_N)$ and the coverage factor, $k_{0.95}$, that gives 95 % coverage probability.

Solution: Since very low counts are possible,

$$u(N_S) = \sqrt{N_S + 1} = 1 \qquad \text{and} \qquad v_{N_S} = 2(N_S + 1) = 2$$
$$u(N_B) = \sqrt{N_B + 1} = 1.732 \qquad \text{and} \qquad v_{N_B} = 2(N_B + 1) = 6$$

Then

$$u_c(R_N) = \sqrt{\frac{u^2(N_S)}{t_S^2} + \frac{u^2(N_B)}{t_B^2}} = \sqrt{\frac{1}{(60{,}000\text{ s})^2} + \frac{3}{(60{,}000\text{ s})^2}} = 3.333 \times 10^{-5}\text{ s}^{-1}$$

$$u_{N_S}(R_N) = \left|\frac{\partial R_N}{\partial N_S}\right| u(N_S) = \frac{1}{t_S}\sqrt{N_S + 1} = \frac{1}{60{,}000\text{ s}} = 1.667 \times 10^{-5}\text{ s}^{-1}$$

$$u_{N_B}(R_N) = \left|\frac{\partial R_N}{\partial N_B}\right| u(N_B) = \frac{1}{t_B}\sqrt{N_B + 1} = \frac{1.732}{60{,}000\text{ s}} = 2.887 \times 10^{-5}\text{ s}^{-1}$$

So, the number of effective degrees of freedom is

$$v_{eff} = \frac{u_c^4(R_N)}{\dfrac{u_{N_S}^4(R_N)}{v_{N_S}} + \dfrac{u_{N_B}^4(R_N)}{v_{N_B}}} = \frac{(3.333 \times 10^{-5})^4}{\dfrac{(1.667 \times 10^{-5})^4}{2} + \dfrac{(2.887 \times 10^{-5})^4}{6}} = 8$$

Then the coverage factor for a 95 % coverage probability is obtained from Table G.2 in Appendix G.

$$k_{0.95} = t_{0.975}(8) = 2.306$$

Notice that in this example, $\nu_{\text{eff}} = \nu_{N_S} + \nu_{N_B}$, but this equality would not hold if the count times for the sample and blank were unequal.

Also notice that the net count rate in this example is negative. Negative results may be common when environmental samples are analyzed for anthropogenic radionuclides.

19D.4 References

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ATTACHMENT 19E
Uncertainties of Mass and Volume Measurements

19E.1 Purpose

This attachment describes methods that may be used to evaluate the measurement uncertainty of a mass or liquid volume measurement. The first purpose of the attachment is to provide methods for more complete evaluations of these uncertainties than those presented earlier in Sections 19.5.9 and 19.5.10. A second purpose is to provide additional examples of uncertainty evaluations, and especially Type A evaluations based on historical data, as described in Section 19.4.2.1.

A third purpose of the attachment is to provide information about the sources of error in mass and volume measurements that may be useful for establishing reasonable quality control criteria. Even if one assumes that weighing and pipetting errors are negligible, the quality control for balances and volumetric apparatus should be strict enough to ensure the assumption is true. Some of the sources of error described below will undoubtedly be considered negligible in many radiochemical measurement processes, yet they may be too large to be ignored in a strict quality control program.

The existence of the attachment is not meant to imply that the uncertainties of mass and volume measurements tend to be relatively important in a radiochemistry laboratory. In fact the relative standard uncertainties of mass and volume measurements tend to be small if the measurements are made properly using appropriate instruments, and they may even be negligible in many cases when compared to other uncertainties associated with radiochemical analysis (e.g., see Section 19.5.12, “Subsampling”). However, one needs to know the performance limits of any measuring instrument. For example the measurement uncertainty may actually be relatively large if a laboratory balance is used to weigh a mass that is too small for it. The uncertainty may also be large in some cases if the sensitivity of the balance varies slightly between tare and gross measurements.

19E.2 Mass Measurements

19E.2.1 Considerations

Regardless of the methods used to evaluate balance measurement uncertainty, the results may be misleading unless the balance is well maintained and protected from external influences, such as drafts and sudden changes in pressure, temperature and humidity.

The appropriate method for evaluating the standard uncertainty of a mass measured using a balance depends on the type of balance, including its principles of calibration and operation, but the uncertainty of the measured result generally has components associated with balance sensitivity,

linearity, repeatability, and air buoyancy. Typically, the component associated with sensitivity includes the uncertainty of calibration and may include variability caused by changing environmental conditions, such as temperature. Other sources of uncertainty may include leveling errors and off-center errors, which should be controlled. Static electrical charges may also have an effect. Changes in mass (e.g., by absorption or evaporation of water) may be very significant for some materials.

19E.2.2 Repeatability

The repeatability of a balance is expressed as a standard deviation and is usually assumed to be independent of the load. It represents the variability of the result of zeroing the balance, loading a mass on the pan, and reading the indication.

Balance manufacturers provide specifications for repeatability, but a test of repeatability should also be part of the routine quality control for the balance (see ASTM E898). The simplest procedure for evaluating repeatability is to make a series of replicate measurements of a mass standard under "repeatability conditions." Repeatability conditions require one balance, one observer, one measurement location, and repetition during a short time period. For each measurement one must zero the balance, load the mass standard, and read the balance indication.

EXAMPLE 19.32 Suppose a laboratory balance has readability 0.0001 g, and, according to the manufacturer, the repeatability is also 0.0001 g. An analyst performs a series of 28 measurements using a 1-gram mass standard to check the repeatability. The results are listed below.

1.0001	0.9996	0.9999	1.0002
1.0002	0.9999	0.9999	1.0001
0.9998	0.9999	1.0000	1.0001
0.9999	0.9999	0.9999	1.0001
0.9998	0.9998	1.0000	0.9998
0.9996	0.9999	0.9999	1.0000
1.0002	0.9999	1.0001	1.0004

The analyst calculates the average, $\overline{W}$, and standard deviation, s, of these values (W_i) as follows.

$$\overline{W} = \frac{1}{28}\sum_{i=1}^{28} W_i = 0.9999607 \text{ g}$$

$$s = \sqrt{\frac{1}{28-1}\sum_{i=1}^{28} (W_i - \overline{W})^2} = 0.00018 \text{ g}$$

So, the analyst evaluates the repeatability to be 0.00018 g.

In this example, since the mass standard is so small, it may not be important that all the measurements be made during a short time period. Environmental factors produce relatively small day-to-day variability in the balance indication, and this variability may not be observable for a 1-gram load. So, the repeatability might be evaluated using the results of 28 routine quality control measurements.

A nested experimental design can also be used to evaluate both the repeatability and the day-to-day (or hour-to-hour) variability due to environmental factors. In this procedure, one makes a series of replicate measurements with the same mass standard each day for a number of days, or perhaps in a morning session and afternoon session each day. Ideally, one should use a mass near the capacity of the balance to obtain the most reliable estimate of day-to-day variability, but almost any mass in the balance's range will do for an estimate of repeatability. The repeatability standard deviation is estimated by

$$s_r = \sqrt{\frac{1}{K(J-1)} \sum_{k=1}^{K} \sum_{j=1}^{J} (x_{k,j} - \bar{x}_k)^2} \tag{19.58}$$

where

s_r is the estimated repeatability standard deviation;
J is the number of repetitions per session;
K is the number of sessions;
$x_{k,j}$ is the j^{th} result obtained in the k^{th} session; and
$\bar{x}_k$ is the average of all the results in the k^{th} session.

The repeatability standard deviation determined by this method is a Type A standard uncertainty with $K(J - 1)$ degrees of freedom.

19E.2.3 Environmental Factors

The correct method for evaluating the balance measurement uncertainty due to environmental factors depends strongly on the method and frequency of calibration. Some balances, especially newer models, have internal calibration masses, which allow frequent calibration with only the push of a button. Other balances use external calibration mass standards and require more care in the calibration process. Balances of the latter type in many cases are calibrated infrequently. If a balance is calibrated immediately before a measurement, then the uncertainty due to environmental factors can be considered to be zero. However, if hours or days pass between the time of calibration and the time of measurement, then this uncertainty component may be significant. For the remainder of this subsection, the latter case is assumed.

Given the nested experimental data from the preceding section, one may estimate the variability due to environmental factors (day-to-day or hour-to-hour variability) as follows.[23]

$$s_{\text{env}}^2 = \frac{1}{K-1}\sum_{k=1}^{K}(\bar{x}_k - \bar{\bar{x}})^2 - \frac{s_{\text{r}}^2}{J} \tag{19.59}$$

where

s_{env}^2 is the estimated variance due to environmental factors and

$\bar{\bar{x}}$ is the grand average of all the data (the average of the $\bar{x}_k$).

If s_{env}^2 is found to be positive, then s_{env} is estimated by its square root; otherwise, s_{env} is assumed to be zero. One estimates the relative component of standard uncertainty of a measured mass due to environmental factors by

$$\varphi_{\text{env}} = \frac{s_{\text{env}}}{m_{\text{check}}} \tag{19.60}$$

where m_{check} is the mass of the standard used in the experiment.

If the variability due to environmental factors is large, its magnitude can also be estimated by weighing a heavy mass standard once per day for a number of days, or perhaps once in the morning and once in the afternoon of each day. Clearly, the observed variability will include the effects of both environmental factors and repeatability, but environmental factors presumably dominate when a heavy mass is weighed, because their effect is proportional to the mass, whereas the repeatability is essentially constant at all masses. So, the observed variability can be used as a reasonable estimate of the variability due to environmental factors alone.

EXAMPLE 19.33 Suppose a laboratory balance has readability 0.0001 g, repeatability 0.0001 g, and a capacity of approximately 110 g. An analyst performs QC measurements using masses of 1, 50, and 100 g. The results obtained using the 100-gram mass standard during a certain time period are as follows:

99.9992	99.9989	99.9986	100.0008
100.0001	99.9990	100.0002	100.0010
99.9993	99.9988	100.0003	99.9975
99.9989	100.0015	99.9989	99.9981
99.9992	99.9992	100.0012	100.0009
100.0002	99.9997	100.0002	100.0005
99.9989	99.9990	100.0011	99.9991

[23] An F-test may be used to test for the presence of variance due to environmental factors. If this variance is zero, then the quantity $Js_{\bar{x}}^2 / s_r^2$, where $s_{\bar{x}}^2$ denotes the experimental variance of the averages $\bar{x}_i$, may be assumed to have an F-distribution with $K - 1$ numerator degrees of freedom and $K(J - 1)$ denominator degrees of freedom.

The average, $\overline{W}$, and standard deviation, $s(W_i)$, of these values are calculated below.

$$\overline{W} = \frac{1}{28}\sum_{i=1}^{28} W_i = 99.9996536 \text{ g}$$

$$s(W_i) = \sqrt{\frac{1}{28-1}\sum_{i=1}^{28}(W_i - \overline{W})^2} = 0.001016 \text{ g}$$

Since this standard deviation is much larger than the repeatability, 0.0001 g, essentially all of the variability may be attributed to environmental factors. The estimate is slightly inflated by the balance's repeatability variance, but the difference in this case is only about 0.5 % of the value shown. So, the relative standard uncertainty due to environmental factors is estimated as

$$\varphi_{\text{env}} = \frac{0.001016}{100} \approx 1.0 \times 10^{-5}$$

19E.2.4 Calibration

The uncertainty of calibration includes components associated with the mass standard or standards, repeatability, and variability due to environmental factors.

When a precision mass standard is used for calibration, the standard uncertainty of its mass is generally negligible. However, the uncertainty may be evaluated if necessary from the specified mass tolerance. For example, a 100-gram ASTM Class-1 mass standard has a tolerance of 0.00025 g, which may be assumed to represent the half-width of a triangular distribution centered at zero (ASTM E617). The standard uncertainty may be found by dividing this tolerance by $\sqrt{6}$ and is approximately 0.00010 g, or 1.0×10^{-6} when expressed in relative terms.

The total relative standard uncertainty of a mass measurement due to calibration may be estimated as follows.

$$\varphi_{\text{cal}} = \sqrt{\varphi_{\text{env}}^2 + \frac{s_{\text{r}}^2 + \delta_{\text{cal}}^2/6}{m_{\text{cal}}^2}} \tag{19.61}$$

where

φ_{cal} is the total relative standard uncertainty of a balance measurement due to calibration;
φ_{env} is the relative standard uncertainty due to environmental factors;
s_{r} is the repeatability standard deviation;
δ_{cal} is the tolerance for the mass of the calibration standard; and
m_{cal} is the mass of the standard used for calibration.

If environmental conditions are not well-controlled, φ_{env} may tend to dominate the other components here, since both s_r and δ_{cal} are much smaller than m_{cal}.

19E.2.5 Linearity

The linearity of a balance should be specified by the manufacturer as a tolerance, a_L, which represents the maximum deviation of the balance indication from the value that would be obtained by linear interpolation between the calibration points. Routine quality control should ensure that the linearity remains within acceptable limits.

The *Eurachem/CITAC Guide: Quantifying Uncertainty in Analytical Measurement* recommends that the linearity tolerance a_L be treated as the half-width of a rectangular distribution and that a_L therefore be divided by $\sqrt{3}$ to obtain the standard uncertainty (Eurachem, 2000). However, since the linearity error is likely to vary as a sinusoidal function of the load, as illustrated in Figure 19.13, the divisor $\sqrt{2}$ may be more appropriate. So, the standard uncertainty due to linearity for a simple mass measurement may be evaluated as $a_L / \sqrt{2}$. Whether one uses $\sqrt{3}$ or the more conservative value $\sqrt{2}$ depends partly on how conservative one believes the estimate of a_L to be.

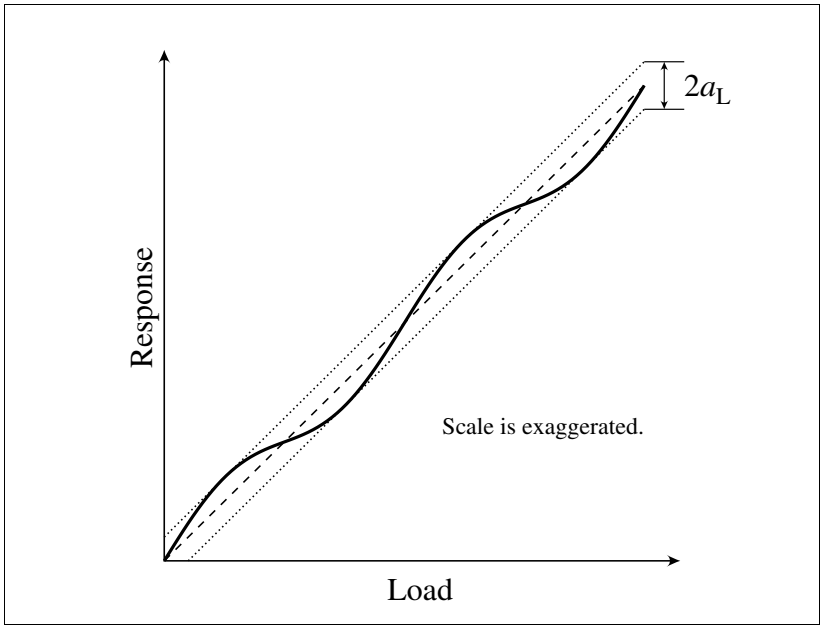

FIGURE 19.13 — Nonlinear balance response curve

19E.2.6 Gain or Loss of Mass

When gain or loss of mass is a relevant issue, as for example when the material being weighed is a volatile liquid or a hygroscopic solid, the mass should be treated as a function of time. One method of determining this function is to weigh the material at different times, recording both the

time and the observed mass, and fit a line or curve to the resulting data points. One can then calculate the mass at a particular time of interest (e.g., before any gain or loss occurred, or perhaps during the period when the material was in a radiation counter). If possible, it is better to weigh the material both before and after the time of interest to avoid extrapolating the curve to points in time where its accuracy may be unknown. However, in some situations extrapolation may be necessary, as for example when determining the dry mass of a hygroscopic precipitate.

The standard uncertainty of a mass calculated in this manner includes components for curve-fitting errors.

19E.2.7 Air-Buoyancy Corrections

Air-buoyancy corrections are not often performed in radiochemistry laboratories, because they are usually negligible in comparison to the overall uncertainty of the result. However, when the measurand is the mass itself and not some other quantity such as a radionuclide concentration whose calculated value depends on the mass, buoyancy corrections may be important. Failure to correct for air buoyancy when weighing water, for example, introduces a relative error of approximately −0.1 %, which may be much larger than the standard uncertainty of the uncorrected mass (e.g., when weighing a gram or more of an aqueous solution on a typical four-place analytical balance).

When a buoyancy-correction factor is used, the true mass is estimated as follows.

$$m = I_{\text{net}}\, B \tag{19.62}$$

where

$$B = \frac{1 - \varrho_{\text{A,C}} / \varrho_{\text{C}}}{1 - \varrho_{\text{A,M}} / \varrho_{\text{M}}} \tag{19.63}$$

and

m is the corrected value for the mass of the material being weighed;
I_{net} is the net balance indication;
B is the buoyancy-correction factor;
ϱ_{M} is the density of the material being weighed;
ϱ_{AM} is the density of the air at the time the material is weighed;
ϱ_{C} is the density of the calibration mass standard; and
ϱ_{AC} is the density of the air at the time of calibration.

The standard uncertainty of B may be obtained as follows.

$$\frac{u^2(B)}{B^2} = \frac{\dfrac{u^2(\varrho_{AC})}{\varrho_{AC}^2} - 2\dfrac{u(\varrho_{AC},\varrho_C)}{\varrho_{AC}\varrho_C} + \dfrac{u^2(\varrho_C)}{\varrho_C^2}}{\left(\dfrac{\varrho_C}{\varrho_{AC}} - 1\right)^2} + \frac{\dfrac{u^2(\varrho_{AM})}{\varrho_{AM}^2} - 2\dfrac{u(\varrho_{AM},\varrho_M)}{\varrho_{AM}\varrho_M} + \dfrac{u^2(\varrho_M)}{\varrho_M^2}}{\left(\dfrac{\varrho_M}{\varrho_{AM}} - 1\right)^2} \tag{19.64}$$

Evaluation of this uncertainty requires estimates of ϱ_M, ϱ_C, ϱ_{AM} and ϱ_{AC} as well as their standard uncertainties and covariances. The covariance $u(\varrho_{AC}, \varrho_C)$ is usually zero or negligible, and $u(\varrho_{AM}, \varrho_M)$ also is usually negligible if the material being weighed is a solid.

Clearly, $u(B)$ tends to be no more significant in a radiochemical measurement than the factor B itself is, but it may generate a large fraction of the uncertainty of the mass, m, since the uncertainty of the mass is often tiny.

The density of air (ϱ_A) depends on temperature, pressure, and humidity, as shown in the following equation.

$$\varrho_A = \varrho_0 \left(\frac{273.15\ \text{K}}{273.15\ \text{K} + t}\right)\left(\frac{p - (0.3783)\varphi e_S}{101.325\ \text{kPa}}\right) \tag{19.65}$$

where

ϱ_A is the density of air;
ϱ_0 is the density of dry air at 0 °C and 101.325 kPa (1 atm);
t is the Celsius temperature;
p is the barometric pressure;
φ is the relative humidity (a fraction between 0 and 1); and
e_S is the saturation vapor pressure of water at temperature t.

The vapor pressure, e_S, is a nonlinear function of t, but it can be approximated by a linear function in the range of temperatures typically encountered in the laboratory. When this approximation is made, the resulting equation for the air density may be written as follows.

$$\varrho_A = \frac{ap - \varphi(bt - c)}{273.15\ \text{K} + t} \tag{19.66}$$

where

a = 3.48589×10^{-3} K · s^2 / m^2;
b = 2.5211151×10^{-4} g / mL; and
c = 2.0590571×10^{-3} K · g / mL.

If p is expressed in kPa and t in °C, then Equation 19.66 with the given numerical values of a, b, and c provides the numerical value of the density, ϱ_A, in $\mathrm{kg/L}$ or $\mathrm{g/mL}$.

Then the standard uncertainty of ϱ_A is given by

$$u(\varrho_A) = \frac{\sqrt{a^2 u^2(p) + (b\varphi + \varrho_A)^2 u^2(t) + (bt - c)^2 u^2(\varphi)}}{273.15\ \mathrm{K} + t} \tag{19.67}$$

The densities of the calibration weight (ϱ_C) and of the solid or liquid material being weighed (ϱ_M) also depend on temperature somewhat, but these temperature effects can usually be safely ignored when calculating the uncertainty of the buoyancy-correction factor, since temperature affects the density of air much more than the density of a solid or liquid.

The effect of pressure on the density of the material being weighed can also usually be neglected. For most practical purposes, the compressibility of a solid or liquid can be considered to be zero.

EXAMPLE 19.34 Suppose the density of the weighed material, ϱ_M, is 0.5 g/mL with a tolerance of 0.2 g/mL, assumed to represent the half-width of a triangular distribution. The density of the calibration mass standard, ϱ_C, is 7.850 g/mL with a tolerance of 0.025 g/mL. Instead of measuring temperature, pressure and humidity at the time of each measurement, the laboratory assumes the following nominal values and tolerances:

Temperature (t)	(22.5 ± 2.5) °C
Pressure (p)	(101.3 ± 2.0) kPa
Relative humidity (φ)	(0.60 ± 0.25)

Recall that

$a = 3.48589 \times 10^{-3}\ \mathrm{K \cdot s^2 / m^2}$;
$b = 2.5211151 \times 10^{-4}\ \mathrm{g / mL}$; and
$c = 2.0590571 \times 10^{-3}\ \mathrm{K \cdot g / mL}$.

Then the air density is calculated as follows.

$$\varrho_{AC} = \varrho_{AM} = \frac{ap - \varphi \times (bt - c)}{273.15\ \text{K} + t}$$

$$= \frac{a \times (101.3\ \text{kPa}) - 0.60 \times (b \times (22.5\ ^\circ\text{C}) - c)}{273.15\ \text{K} + 22.5\ ^\circ\text{C}}$$

$$= \frac{(0.353121\ \text{K} \cdot \text{g/mL}) - (0.002168\ \text{K} \cdot \text{g/mL})}{295.65\ \text{K}}$$

$$= \frac{0.350953\ \text{K} \cdot \text{g/mL}}{295.65\ \text{K}}$$

$$= 1.1871 \times 10^{-3}\ \text{g/mL}$$

(For convenience, unit symbols will be omitted from intermediate steps in the equations below.)

If each of the tolerances for t, p, and φ represents the half-width of a triangular distribution, then

$$u^2(t) = \frac{2.5^2}{6} = 1.04, \qquad u^2(p) = \frac{2.0^2}{6} = 0.667, \qquad \text{and} \qquad u^2(\varphi) = \frac{0.25^2}{6} = 0.0104$$

So, the standard uncertainties of ϱ_{AC} and ϱ_{AM} are

$$u(\varrho_{AC}) = u(\varrho_{AM}) = \frac{\sqrt{a^2 u^2(p) + (b\varphi + \varrho_A)^2 u^2(t) + (bt - c)^2 u^2(\varphi)}}{273.15 + t}$$

$$= \frac{\sqrt{a^2(0.667) + (b \times 0.60 + 1.1871 \times 10^{-3})^2(1.04) + (b \times 22.5 - c)^2(0.0104)}}{273.15 + 22.5}$$

$$= 1.08 \times 10^{-5}\ \text{g/mL}$$

Then the buoyancy-correction factor is

$$B = \frac{1 - \varrho_{AC} / \varrho_C}{1 - \varrho_{AM} / \varrho_M} = \frac{1 - (1.1871 \times 10^{-3} / 7.85)}{1 - (1.1871 \times 10^{-3} / 0.5)} = 1.00223$$

The tolerances for the densities ϱ_C and ϱ_M are the half-widths of triangular distributions; so,

$$u^2(\varrho_C) = \frac{0.025^2}{6} \qquad \text{and} \qquad u^2(\varrho_M) = \frac{0.2^2}{6}$$

The covariances $u(\varrho_{AC}, \rho_C)$ and $u(\varrho_{AM}, \varrho_M)$ are zero in this example. So, the standard uncertainty of B is

$$u(B) = B\sqrt{\frac{u^2(\varrho_{AC})/\varrho_{AC}^2 + u^2(\varrho_C)/\varrho_C^2}{(\varrho_C/\varrho_{AC}-1)^2} + \frac{u^2(\varrho_{AM})/\varrho_{AM}^2 + u^2(\varrho_M)/\varrho_M^2}{(\varrho_M/\varrho_{AM}-1)^2}}$$

$$= 1.00223\sqrt{\frac{(1.08\times10^{-5})^2}{(1.1871\times10^{-3})^2} + \frac{0.025^2/6}{7.85^2}}{\left(\frac{7.85}{1.1871\times10^{-3}}-1\right)^2} + \frac{\frac{(1.08\times10^{-5})^2}{(1.1871\times10^{-3})^2} + \frac{0.2^2/6}{0.5^2}}{\left(\frac{0.5}{1.1871\times10^{-3}}-1\right)^2}}$$

$$= 3.9\times10^{-4}$$

Thus, the buoyancy-correction factor increases the result of the measurement by about 0.2 % and generates a relative standard uncertainty component of approximately 0.04 %. An examination of the calculation reveals that the uncertainty of B in this case is dominated by the uncertainty of ρ_M, the density of the material being weighed. Note that the uncertainty of B is very small and would generally be considered negligible in the final result of a radiochemistry measurement, but it may represent a significant fraction of the uncertainty of the mass measurement.

19E.2.8 Combining the Components

When the balance is used to measure the mass, m, of an object placed on the pan, the mass is given by $m = IB$, and its standard uncertainty by

$$u(m) = \sqrt{B^2\left(I^2(\varphi_{cal}^2 + \varphi_{env}^2) + \frac{a_L^2}{2} + s_r^2\right) + I^2u^2(B)} \qquad (19.68)$$

where

m	is the buoyancy-corrected mass;
I	is the balance indication;
B	is the buoyancy-correction factor[24];
φ_{cal}	is the relative standard uncertainty due to calibration;
φ_{env}	is the relative standard uncertainty due to environmental factors;

[24] Variations in temperature, humidity, and pressure may produce a correlation between the buoyancy-correction factor, B, and the balance indication, I, because of the influence of environmental factors on the balance's sensitivity. The correlation is assumed here to be negligible.

a_L is the linearity tolerance; and
s_r is the repeatability standard deviation.

Often the balance is used to weigh material in a container. The balance is zeroed with the empty container on the pan and the container is then filled and weighed. In this case the linearity uncertainty component is counted twice, because the linearity error is assumed to vary between the two loads. (This assumption tends to be conservative when small masses are weighed.) Although the buoyancy factors for the container and its contents may differ because of the different densities of the materials, the only value of B that is used is the buoyancy factor for the material being weighed.

In a third scenario the empty container is weighed, removed from the pan, and then filled with material. The balance is zeroed again, and the filled container is weighed. In this case both the linearity and repeatability components of uncertainty must be counted twice, because two distinct measurements are made. So, the corrected net mass and its standard uncertainty are

$$\begin{aligned} m &= I_{\text{net}} B \\ u(m) &= \sqrt{B^2\left(I_{\text{net}}^2(\varphi_{\text{cal}}^2 + \varphi_{\text{env}}^2) + a_L^2 + 2s_r^2\right) + I_{\text{net}}^2 u^2(B)} \end{aligned} \tag{19.69}$$

where
I_{net} is the net balance indication (gross − tare) and
B is the buoyancy factor for the material being weighed.

In a variant of the third scenario, the same weighing procedure is used but there is a significant time delay between the tare and gross measurements, which allows environmental conditions to change and the balance sensitivity to drift. In this case the mass and its standard uncertainty should be calculated as follows.

$$\begin{aligned} m &= I_{\text{net}} B \\ u(m) &= \sqrt{B^2\left(I_{\text{net}}^2\varphi_{\text{cal}}^2 + (I_{\text{tare}}^2 + I_{\text{gross}}^2)\varphi_{\text{env}}^2 + a_L^2 + 2s_r^2\right) + I_{\text{net}}^2 u^2(B)} \end{aligned} \tag{19.70}$$

where I_{tare} and I_{gross} denote the balance indications for the tare and gross measurements, respectively. In this scenario the uncertainty due to environmental effects may be relatively large if the tare mass is large relative to the net. When this is true, the analyst should consider measuring and correcting for the sensitivity drift.

19E.3 Volume Measurements

Section 19.5.10 presents a simplified approach to the evaluation of the uncertainty of a volume measurement, which may be adequate for most purposes in a typical radiochemistry laboratory.

This section describes experimental methods for evaluating the uncertainty components described in Section 19.5.10 and also considers additional uncertainty components.

The density of a liquid depends on its temperature. For this reason, when a volume is measured, it may be important whether the volume of interest is the volume at the current room temperature, the long-term mean room temperature, or some other temperature, such as 20 °C. However, one should determine whether the effect of temperature is really significant for the measurement, since temperature effects are usually very small.

If the quantity of interest is the volume at room temperature when the volume is measured, the effects of temperature can usually be ignored. The following discussion assumes that the quantity of interest is the volume at the mean room temperature and that the actual room temperature may fluctuate within specified limits.

Three approaches to uncertainty evaluation for volume measurements are discussed. The following uncertainty components are considered:

- The capacity of the measuring device,
- Repeatability,
- The analyst's bias in using the device (e.g., reading a meniscus), and
- Temperature effects.

19E.3.1 First Approach

The first approach considered here is appropriate for volumetric glassware. Example 19.26 in Section 19.5.10 illustrates this approach using only the uncertainty components associated with capacity and repeatability, which tend to be dominant.

CAPACITY

The capacity of a volumetric pipet or flask (at 20 °C) is generally specified with a tolerance, δ_{cap}, which may be assumed to represent the half-width of a rectangular or triangular distribution (e.g., see ASTM E288 and ASTM E969). The Eurachem/CITAC Guide recommends a triangular distribution, which is based on the assumption that values near the nominal value are more likely than those near the extremes (Eurachem, 2000). Using a triangular distribution, one evaluates the uncertainty component of the volume associated with the capacity as $\delta_{cap} / \sqrt{6}$.

REPEATABILITY

As described in Section 19.5.10, one may evaluate the uncertainty associated with precision, or repeatability, for volumetric glassware by obtaining the dimensions of the glassware and estimating the maximum "possible" deviation of the meniscus from the capacity line. ASTM E969,

"Standard Specification for Glass Volumetric (Transfer) Pipets," specifies that the internal cross-section of any Class A or Class B pipet must be circular, and provides ranges of permissible internal diameters at the capacity mark. If d denotes the actual diameter and δ_{men} denotes the maximum deviation of the meniscus from the capacity mark, then the maximum deviation of the volume from its value at the capacity mark is given by

$$\delta_{rep} = \frac{\pi \delta_{men} d^2}{4} \tag{19.71}$$

When δ_{men} and d are expressed in centimeters, Equation 19.71 gives the maximum volume deviation, δ_{rep}, in milliliters. Then if δ_{men} is assumed to represent the half-width of a triangular distribution, the standard uncertainty of the volume due to repeatability is $\delta_{rep} / \sqrt{6}$, which equals

$$\frac{\pi \delta_{men} d^2}{4\sqrt{6}}.$$

ANALYST'S BIAS

A similar method can be used to evaluate the uncertainty due to the analyst's bias in reading the meniscus. One estimates the maximum possible *systematic* error in the height of the meniscus, δ_{sys}, and evaluates the associated uncertainty component of the volume as

$$\frac{\pi \delta_{sys} d^2}{4\sqrt{6}}.$$

Presumably the value of δ_{sys} should be only a fraction of that of δ_{men}; so, this uncertainty should contribute little to the total uncertainty of a single volume measurement, although it may be relatively more significant if the glassware is used to dispense several aliquants of liquid in a single experiment.

TEMPERATURE EFFECTS

Temperature influences a volume measurement through its effects on the density of the liquid and the capacity of the glassware. Both effects tend to be very small and can often be ignored.

Volumetric glassware is calibrated at 20 °C, but the glassware expands with increasing temperature. For most purposes the effect of temperature on capacity can be ignored, because it is much smaller than the effect on the density of the liquid. For example, the capacity of ASTM Type I, Class A, borosilicate glassware increases by only about 0.001 % for each degree Celsius of tem-

perature increase. Temperature effects on softer materials, such as plastic, may be more significant; however, soft plastic volumetric ware is seldom used when high accuracy is required.

The glassware's capacity at room temperature may be approximated by

$$V_t = V_{20}(1 + \alpha_V(t - 20\ ^\circ\text{C})) \tag{19.72}$$

where

t is the room temperature (Celsius);
V_t is the capacity at temperature t;
V_{20} is the nominal capacity at 20 °C; and
α_V is the glassware's coefficient of thermal cubical expansion.

Table 19.5, which is taken from ASTM E542, lists values of α_V for materials often used in volumetric ware. The referenced document does not provide the uncertainties of these values, but relative tolerances of ±10 % (triangular distribution) seem reasonable. The actual uncertainty is likely to be insignificant to the analyst.

TABLE 19.5 — Coefficients of cubical expansion

Material	Coefficient of cubical expansion, $°C^{-1}$
Fused silica (quartz)	0.0000016
Borosilicate glass (Type I, Class A)	0.000010
Borosilicate glass (Type I, Class B)	0.000015
Soda-lime glass	0.000025
Polypropylene plastic	0.000240
Polycarbonate plastic	0.000450
Polystyrene plastic	0.000210

Example 19.35 An analyst uses a 1-milliliter ASTM Type I, Class A borosilicate glass pipet to dispense an aliquant of a solution when the room temperature is approximately 22.5 °C. The actual volume dispensed is estimated to be

$$V_t = (1\ \text{mL})(1 + (0.000010\ ^\circ\text{C}^{-1})(22.5\ ^\circ\text{C} - 20\ ^\circ\text{C})) = 1.000025\ \text{mL}$$

The analyst considers the temperature correction and its uncertainty in this case to be negligible.

The standard uncertainty due to temperature effects on the liquid's density may be derived from a temperature range, $t \pm \delta_{tem}$, and the liquid's coefficient of thermal expansion, β, at the center of the range. Assuming a triangular distribution for the temperature with half-width δ_{tem}, the relative standard uncertainty component due to temperature variations is $|\beta|\,\delta_{tem}/\sqrt{6}$. At typical room temperatures the value of β for water lies in the range 0.00021 °C^{-1} to 0.00026 °C^{-1}; so, the total standard uncertainty due to temperature effects is generally less than 0.05 %, which can often be considered negligible. Values of β for water may also be applied to dilute aqueous solutions. Other liquids have different coefficients of thermal expansion.

Example 19.36 An analyst measures a volume of dilute HCl in a laboratory where the temperature range is assumed to be (22.5 ± 2.0) °C. The coefficient of thermal expansion for water at 22.5 °C is approximately 0.00023 °C^{-1}. So, the relative standard uncertainty of the volume due to temperature effects on the density of the solution is

$$|0.00023\ ^\circ\mathrm{C}^{-1}|\frac{2.0\ ^\circ\mathrm{C}}{\sqrt{6}} = 0.00019$$

Again, the analyst considers the uncertainty due to temperature (0.02 %) to be negligible.

19E.3.2 Second Approach

An alternative approach, which is suitable for most varieties of pipets, is to calibrate the device gravimetrically using an analytical balance. The balance, to be useful, must provide better accuracy than the pipet. In particular the balance's repeatability and linearity tolerances should be small relative to the tolerances for the pipet. The calibration provides an estimate of the pipet's capacity, the standard uncertainty of the capacity, and the variability to be expected during use. The procedure involves dispensing a series of n pipet volumes of a specified liquid into a container and weighing the container and zeroing the balance after each volume is added. Usually the container must have a small mouth to reduce evaporation. The temperature of the room, the liquid, and the apparatus involved should be specified, equilibrated, and controlled during the experiment. The calibration is most often performed using water.

The procedure produces a set of balance indications, I_i, from which the arithmetic mean, $\bar{I}$, and the experimental standard deviation, $s(I_i)$, are calculated. To obtain the estimated mean pipet volume, V, the mean balance indication, $\bar{I}$, is multiplied by a factor, Z, which equals the quotient of the buoyancy-correction factor and the density of the liquid at room temperature. So, v is given explicitly by

$$V = \bar{I}Z \qquad \text{where} \qquad Z = \frac{1 - \varrho_{AC}/\varrho_C}{\varrho_M - \varrho_{AM}} \tag{19.73}$$

and where

ϱ_M is the density of the liquid;
ϱ_{AM} is the density of the air at the time the liquid is weighed;
ϱ_C is the density of the calibration mass standard for the balance; and
ϱ_{AC} is the density of the air at the time of the balance calibration.

A correction factor for thermal expansion of the pipet may also be included, if desired.

ASTM E542, "Standard Practice for Calibration of Laboratory Volumetric Apparatus," provides additional information about the procedure, including tables of values of Z for various conditions. Table 19.6, which is taken from ASTM E542, shows the density of air-free water at various temperatures.[25] Section 19E.2.7 of this attachment describes an equation to calculate the density of air as a function of temperature, pressure, and humidity.

TABLE 19.6 — Density of air-free water

Temperature, °C	Density, g / cm^3	Temperature, °C	Density, g / cm^3
15	0.999098	26	0.996782
16	0.998941	27	0.996511
17	0.998773	28	0.996232
18	0.998593	29	0.995943
19	0.998403	30	0.995645
20	0.998202	31	0.995339
21	0.997990	32	0.995024
22	0.997768	33	0.994701
23	0.997536	34	0.994369
24	0.997294	35	0.994030
25	0.997043		

The volume, V, estimated by the calibration may be substituted for the pipet's nominal capacity when the pipet is used later in an analytical measurement. The uncertainty of V as a predictor of the volume that will be dispensed during a subsequent measurement may be calculated as

[25] The densities in the table are approximated adequately (to six decimal places) by the rational function

$$\varrho = \frac{0.999924794 + 7.37771644 \times 10^{-3}(t) - 7.52261541 \times 10^{-6}(t^2)}{1 + 7.3265954 \times 10^{-3}(t)}$$

where ϱ denotes density in g/cm^3 and t denotes temperature in °C. Use of this equation allows calculation of the coefficient of thermal expansion, β, since $\beta = -(d\varrho / dt) / \varrho$.

$$u(V) = \sqrt{Z^2 s^2(I_i)\left(1 + \frac{1}{n}\right) + V^2\left(\varphi_{\text{cal}}^2 + \varphi_{\text{env}}^2 + \frac{\beta^2 \delta_{\text{tem}}^2}{3}\right)} \tag{19.74}$$

where $s(I_i)$ denotes the experimental standard deviation of the n balance indications, φ_{cal} and φ_{env} denote the relative standard uncertainties of mass measurements associated with balance calibration and environmental factors, respectively (see Section 19E.2), δ_{tem} denotes the temperature tolerance, and β denotes the liquid's coefficient of thermal expansion. Note that the uncertainty of the buoyancy-correction factor has been ignored here and the standard uncertainty of Z has been equated with the component due to thermal expansion of the liquid, which is assumed to be dominant. The temperature distribution is taken to be triangular. Also note that the correlation between Z and $\bar{I}$ induced by temperature effects on both the liquid's density and the balance sensitivity is unknown and has been ignored. Given the typical magnitudes of the various uncertainty components here, the following uncertainty estimate is likely to be adequate for most purposes (a pure Type A evaluation with $n - 1$ degrees of freedom).

$$u(V) = Z s(I_i)\sqrt{1 + \frac{1}{n}} \tag{19.75}$$

Note that if a different analyst performs the measurement, there may be an additional uncertainty component associated with the difference in individual techniques.

If the mean volume is within specified tolerances, a slightly simplified approach is possible. The pipet's nominal capacity may be used as the volume, V, and the tolerance, δ_{cap}, may be used in a Type B evaluation of standard uncertainty. In this case, the standard uncertainty of V is evaluated as shown below.

$$u(V) = \sqrt{\frac{\delta_{\text{cap}}^2}{6} + Z^2 s^2(I_i) + \frac{V^2 \beta^2 \delta_{\text{tem}}^2}{6}} \tag{19.76}$$

Again, given the typical magnitudes of the uncertainty components, the following simpler expression is usually adequate.

$$u(V) = \sqrt{\frac{\delta_{\text{cap}}^2}{6} + Z^2 s^2(I_i)} \tag{19.77}$$

The experimental procedure outlined above may also be adapted for other volume measuring devices, including flasks and graduated cylinders.

19E.3.3 Third Approach

The manufacturers of certain types of pipetting devices (e.g., Eppendorf® pipettes) provide specifications for bias and precision. For these devices, the manufacturer's specifications for bias and precision may be assumed, provided the analyst uses the device properly, according to the manufacturer's directions. In this case the Type B standard uncertainty of a pipetted volume, V, is evaluated as

$$u(V) = \sqrt{\frac{\delta_{\text{cap}}^2}{6} + s^2 + \frac{V^2 \beta^2 \delta_{\text{tem}}^2}{6}} \tag{19.78}$$

where δ_{cap} is the manufacturer's stated bias tolerance, assumed to represent the half-width of a triangular distribution, s is the stated standard deviation, β is the liquid's coefficient of thermal expansion, and δ_{tem} is the temperature tolerance. This approach has the advantage of simplicity; however, if the analyst fails to follow the manufacturer's directions for use, the uncertainty estimate given by Equation 19.78 may be unrealistic. (As in the preceding section, the uncertainty due to temperature effects can usually be ignored.)

Either of the first two approaches described above may also be used for these devices.

19E.4 References

American Society for Testing and Materials (ASTM) E617. *Standard Specification for Laboratory Weights and Precision Mass Standards*. West Conshohocken, PA. 1991.

American Society for Testing and Materials (ASTM) E898. *Standard Method of Testing Top-Loading, Direct-Reading Laboratory Scales and Balances*. West Conshohocken, PA. 1993.

American Society for Testing and Materials (ASTM) E288. *Standard Specification for Laboratory Glass Volumetric Flasks*. West Conshohocken, PA. 1994.

American Society for Testing and Materials (ASTM) E969. *Standard Specification for Glass Volumetric (Transfer) Pipets*. West Conshohocken, PA. 1995.

American Society for Testing and Materials (ASTM) E542. *Standard Practice for Calibration of Laboratory Volumetric Glassware*. West Conshohocken, PA. 2000.

Eurachem. 2000. *Eurachem/CITAC Guide: Quantifying Uncertainty in Analytical Measurement*, 2nd ed. Eurachem.

20 DETECTION AND QUANTIFICATION CAPABILITIES

20.1 Overview

This chapter discusses issues related to analyte detection and quantification capabilities. The topics addressed include methods for deciding whether an analyte is present in a sample as well as measures of the detection and quantification capabilities of a measurement process.

Environmental radioactivity measurements may involve material containing very small amounts of the radionuclide of interest. Measurement uncertainty often makes it difficult to distinguish such small amounts from zero. So, an important performance characteristic of an analytical measurement process is its *detection capability*, which is usually expressed as the smallest concentration of analyte that can be reliably distinguished from zero. Effective project planning requires knowledge of the detection capabilities of the analytical procedures that will be or could be used. This chapter explains the performance measure, called the *minimum detectable concentration* (MDC), or the *minimum detectable amount* (MDA), that is used to describe radioanalytical detection capabilities, as well as some proper and improper uses for it. The chapter also gives laboratory personnel methods for calculating the minimum detectable concentration.

Project planners may also need to know the *quantification capability* of an analytical procedure, or its capability for precise measurement. The quantification capability is expressed as the smallest concentration of analyte that can be measured with a specified relative standard deviation. This chapter explains a performance measure called the *minimum quantifiable concentration* (MQC), which may be used to describe quantification capabilities. (See Chapter 3 and Appendix C for explanations of the role of the minimum detectable concentration and minimum quantifiable concentration in the development of measurement quality objectives.)

Section 20.2 presents the concepts and definitions used throughout the chapter. The major recommendations of the chapter are listed in Section 20.3. Section 20.4 presents the mathematical details of calculating critical values, minimum detectable values, and minimum quantifiable values. Attachment 20A describes issues related to analyte detection decisions in low-background radiation counting and how the issues may be dealt with mathematically.

20.2 Concepts and Definitions

Contents

20.2.1 Analyte Detection Decisions

An obvious question to be answered following the analysis of a laboratory sample is: "Does the sample contain a positive amount of the analyte?" Uncertainty in the measured value

often makes the question difficult to answer. There are different methods for making a *detection decision*, but the methods most often used in radiochemistry involve the principles of statistical hypothesis testing.

To "detect" the analyte in a laboratory sample means to decide on the basis of the measurement data that the analyte is present. The detection decision involves a choice between two hypotheses about the sample. The first hypothesis is the "null hypothesis" H_0: The sample is analyte-free. The second hypothesis is the "alternative hypothesis" H_1: The sample is not analyte-free. The null hypothesis is presumed to be true unless there is sufficient statistical evidence to the contrary. If the evidence is strong enough, the null hypothesis is rejected in favor of the alternative hypothesis. (See Attachment 3B of Chapter 3 for an introduction to these concepts.)

The methods of statistical hypothesis testing do not guarantee correct decisions. In any hypothesis test there are two possible types of decision errors. An error of the first type, or Type I error, occurs if one rejects the null hypothesis when it is true. An error of the second type, or Type II error, occurs if one fails to reject the null hypothesis when it is false. The probability of a Type I error is usually denoted by α, and the probability of a Type II error is usually denoted by β. In the context of analyte detection decisions, to make a Type I error is to conclude that a sample contains the analyte when it actually does not, and to make a Type II error is to fail to conclude that a sample contains the analyte when it actually does.[1]

A Type I error is sometimes called a "false rejection" or "false positive," and a Type II error is sometimes called a "false acceptance" or "false negative." Recently the terms "false positive" and "false negative" have been losing favor, because they can be misleading in some contexts.

The use of statistical hypothesis testing to decide whether an analyte is present in a laboratory sample is conceptually straightforward, yet the subject still generates confusion and disagreement among radiochemists and project managers. Hypothesis testing has been used for analyte detection in radiochemistry at least since 1962. Two influential early publications on the subject were Altshuler and Pasternack (1963) and Currie (1968). Other important but perhaps less well-known documents were Nicholson (1963 and 1966). Most approaches to the detection problem have been similar in principle, but there has been inadequate standardization of terminology and methodology. However, there has been recent progress. In 1995, the International Union of Pure and Applied Chemistry (IUPAC) published "Nomenclature in Evaluation of Analytical Methods Including Detection and Quantification Capabilities" (IUPAC, 1995), which recommends a uniform approach to defining various performance characteristics of any chemical measurement process, including detection and quantification limits; and in 1997 the International Organization for Standardization (ISO) issued the first part of ISO 11843 "Capability of Detection," a multi-

[1] Note that in any given situation, only one of the two types of decision error is possible. If the sample *does not* contain the analyte, a Type I error is possible. If the sample *does* contain the analyte, a Type II error is possible.

part standard which deals with issues of detection in an even more general context of measurement. Part 1 of ISO 11843 includes terms and definitions, while Parts 2–4 deal with methodology. Although members of the IUPAC and ISO working groups collaborated during the development of their guidelines, substantial differences between the final documents remain. MARLAP follows both the ISO and IUPAC guidelines where they agree but prefers the definitions of ISO 11843-1 for the critical value and minimum detectable value, relating them to the terminology and methodology already familiar to most radiochemists.

In July 2000, ISO also published the first three parts of ISO 11929 "Determination of the Detection Limit and Decision Threshold for Ionizing Radiation Measurements." Unfortunately, ISO 11929 is not completely consistent with either the earlier ISO standard or the IUPAC recommendations.

In the terminology of ISO 11843-1, the analyte concentration of a laboratory sample is the *state variable*, denoted by Z, which represents the state of the material being analyzed. Analyte-free material is said to be in the *basic state*. The state variable cannot be observed directly, but it is related to an observable *response variable*, denoted by Y, through a *calibration function* F, the mathematical relationship being written as $Y = F(Z)$. In radiochemistry, the response variable Y is most often an instrument signal, such as the number of counts observed. The inverse, F^{-1}, of the calibration function is sometimes called the *evaluation function* (IUPAC, 1995). The evaluation function, which gives the value of the net concentration in terms of the response variable, is closely related to the *mathematical model* described in Section 19.4.2 of Chapter 19.

The difference between the state variable, Z, and its value in the basic state is called the *net state variable*, which is denoted by X. In radiochemistry there generally is no difference between the state variable and the net state variable, because the basic state is represented by material whose analyte concentration is zero. In principle the basic state might correspond to a positive concentration, but MARLAP does not address this scenario.

20.2.2 The Critical Value

In an analyte detection decision, one chooses between the null and alternative hypotheses on the basis of the observed value of the response variable, Y. The value of Y must exceed a certain threshold value to justify rejection of the null hypothesis and acceptance of the alternative: that the sample is not analyte-free. This threshold is called the *critical value* of the response variable and is denoted by y_C.

The calculation of y_C requires the choice of a *significance level* for the test. The significance level is a specified upper bound for the probability, α, of a Type I error (false rejection). The significance level is usually chosen to be 0.05. This means that when an analyte-free sample is analyzed, there should be at most a 5 % probability of incorrectly deciding that the analyte is present. In principle other values of α are possible, but in the field of radiochemistry, α is often

implicitly assumed to be 0.05. So, if another value is used, it should be explicitly stated. A smaller value of α makes type I errors less likely, but also makes Type II errors more likely when the analyte concentration in the laboratory sample is positive but near zero.

The *critical value of the analyte concentration*, x_C, as defined by MARLAP, is the value obtained by applying the evaluation function, F^{-1}, to the critical value of the response variable, y_C. Thus, $x_C = F^{-1}(y_C)$. In radiochemistry, when y_C is the gross instrument signal, this formula typically involves subtraction of the blank signal and division by the counting efficiency, test portion size, chemical yield, decay factor, and possibly other factors. In ANSI N42.23, "Measurement and Associated Instrument Quality Assurance for Radioassay Laboratories," the same value, x_C, is called the *decision level concentration*, or DLC.

A detection decision can be made by comparing the observed gross instrument signal to its critical value, y_C, as indicated above. However, it has become standard practice in radiochemistry to make the decision by comparing the *net* instrument signal to its critical value, S_C. The net signal is calculated from the gross signal by subtracting the estimated blank value and any interferences. The critical net signal, S_C, is calculated from the critical gross signal, y_C, by subtracting the same correction terms; so, in principle, either approach should lead to the same detection decision.

Since the term "critical value" alone is ambiguous, one should specify the variable to which the term refers. For example, one may discuss the critical (value of the) analyte concentration, the critical (value of the) net signal, or the critical (value of the) gross signal.

It is important to understand that there is no single equation for the critical value that is appropriate in all circumstances. Which equation is best depends on the structure of the measurement process and the statistics of the measurements. Many of the commonly used expressions are based on the assumption of Poisson counting statistics and are invalid if that assumption is not a good approximation of reality. For example, if the instrument background varies between measurements or if it is necessary to correct the result for sample-specific interferences, then expressions for the critical value based on the Poisson model require modification or replacement. If the analyte is a naturally occurring radionuclide that is present at varying levels in reagents, then a correction for the reagent contamination is necessary and expressions based on the Poisson model may be completely inappropriate. In this case the critical value usually must be determined by repeated measurements of blanks under conditions similar to those of the sample measurement.

Generally, the clients of a laboratory do not have the detailed knowledge of the measurement process that is necessary to choose a specific equation for the critical value; however, clients may specify the desired Type I error rate (5 % by default).

Section 20.4.1 and Section 20A.2 of Attachment 20A provide more information on the calculation of critical values.

20.2.3 The Blank

In radiochemistry, the response variable is typically an instrument signal, whose mean value generally is positive even when analyte-free material is analyzed. The gross signal must be corrected by subtracting an estimate of the signal produced by analyte-free material. This estimate may be obtained by means of any of several types of radiochemical blanks, including blank sources and reagent blanks (Chapter 18). The radiochemical blank is chosen to provide an estimate of the mean signal produced by an analyte-free sample, whether the signal is produced by the instrument background, contaminated reagents, or other causes. The most appropriate type of blank depends on the analyte and on the method and conditions of measurement. Some analytes. including many anthropogenic radionuclides, are unlikely to occur as contaminants in laboratory reagents. For these analytes the radiochemical blank may be only a blank source that mimics the container, geometry, and physical form of a source prepared from a real sample. On the other hand, many naturally occurring radionuclides may be present in laboratory water, reagents, and glassware, and these analytes often require the laboratory to analyze reagent blanks or matrix blanks to determine the distribution of the instrument signal that can be expected when analyte-free samples are analyzed.

20.2.4 The Minimum Detectable Concentration

The *power* of any hypothesis test is defined as the probability that the test will reject the null hypothesis when it is false.[2] So, if the probability of a Type II error is denoted by β, the power is $1 - \beta$. In the context of analyte detection, the power of the test is the probability of correctly detecting the analyte (concluding that the analyte is present), which happens whenever the response variable exceeds its critical value. The power depends on the analyte concentration of the sample and other conditions of measurement; so, one often speaks of the "power function" or "power curve." Note that the power of a test for analyte detection generally is an increasing function of the analyte concentration — i.e., the greater the analyte concentration the higher the probability of detecting it.

The *minimum detectable concentration* (MDC) is the minimum concentration of analyte that must be present in a sample to give a specified power, $1 - \beta$. It may also be defined as:

- The minimum analyte concentration that must be present in a sample to give a specified probability, $1 - \beta$, of detecting the analyte; or

[2] Some authors define *power* more simply as the probability that the null hypothesis will be rejected — regardless of whether it is true or false. However, the concept of power is more relevant when the null hypothesis is false.

- The minimum analyte concentration that must be present in a sample to give a specified probability, $1 - \beta$, of measuring a response greater than the critical value, leading one to conclude correctly that there is analyte in the sample.

The value of β that appears in the definition, like α, is usually chosen to be 0.05 or is assumed to be 0.05 by default if no value is specified. The minimum detectable concentration is denoted in mathematical expressions by x_D. In radiochemistry the MDC is usually obtained from the *minimum detectable value of the net instrument signal*, S_D, which is the smallest mean value of the net signal at which the probability that the response variable will exceed its critical value is $1 - \beta$. The relationship between the critical net signal, S_C, and the minimum detectable net signal, S_D, is shown in Figure 20.1.

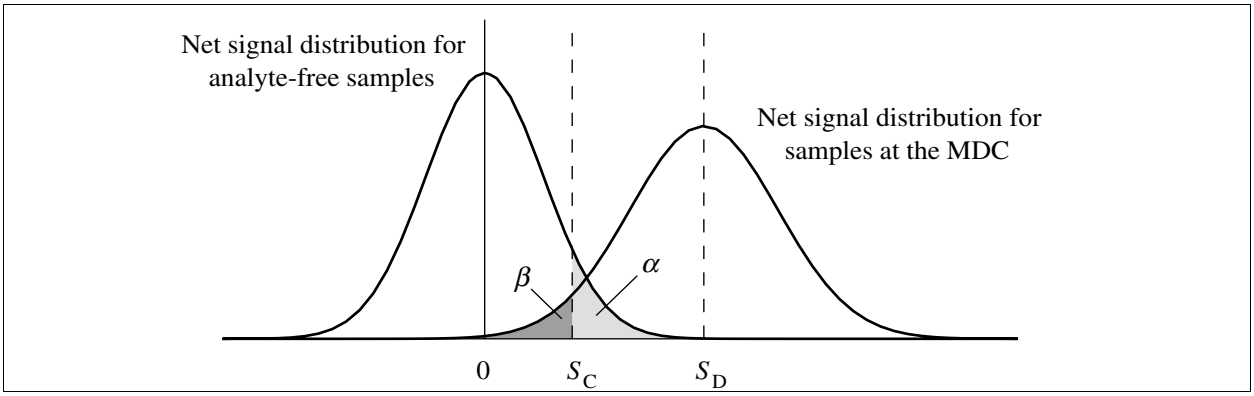

FIGURE 20.1 — The critical net signal, S_C, and minimum detectable net signal, S_D

Sections 20.4.2 and 20A.3 provide more information about the calculation of the minimum detectable concentration.

The minimum detectable value of the activity or mass of analyte in a sample is sometimes called the *minimum detectable amount*, which may be abbreviated as MDA (ANSI N13.30 and N42.23). This chapter focuses on the MDC, but with few changes the guidance is also applicable to any type of MDA.

While project planners and laboratories have some flexibility in choosing the significance level, α, used for detection decisions, the MDC is usually calculated with $\alpha = \beta = 0.05$. The use of standard values for α and β allows meaningful comparison of analytical procedures.

The MDC concept has generated controversy among radiochemists for years and has frequently been misinterpreted and misapplied. The term must be carefully and precisely defined to prevent confusion. The MDC is by definition an estimate of the *true* concentration of analyte required to give a specified high probability that the *measured* response will be greater than the critical

value. Thus, the common practice of comparing a measured concentration to the MDC to make a detection decision is incorrect.

There are still disagreements about the proper uses of the MDC concept. Some define the MDC strictly as an estimate of the nominal detection capability of a *measurement process*. Those in this camp consider it invalid to compute an MDC for each *measurement* using sample-specific information such as test portion size, chemical yield, and decay factors (e.g., ANSI N42.23). The opposing view is that the "sample-specific" MDC is a useful measure of the detection capability of the measurement process, not just in theory, but as it actually performs. The sample-specific MDC may be used, for example, to determine whether an analysis that has failed to detect the analyte of interest should be repeated because it did not have the required or promised detection capability.

Neither version of the MDC can legitimately be used as a threshold value for a detection decision. The definition of the MDC presupposes that an appropriate detection threshold (i.e., the critical value) has already been defined.

Many experts strongly discourage the reporting of a sample-specific MDC because of its limited usefulness and the likelihood of its misuse. Nevertheless, this practice has become firmly established at many laboratories and is expected by many users of radioanalytical data. Furthermore, NUREG/CR-4007 states plainly that "the critical (decision) level and detection limit [MDC] really do vary with the nature of the sample" and that "proper assessment of these quantities demands relevant information on each sample, unless the variations among samples (e.g., interference levels) are quite trivial" (NRC, 1984).

Since a sample-specific MDC is calculated from measured values of input quantities such as the chemical yield, counting efficiency, test portion size, and background level, the MDC estimate has a combined standard uncertainty, which in principle can be obtained by uncertainty propagation (see Chapter 19).

In the calculation of a sample-specific MDC, the treatment of any *randomly varying but precisely measured* quantities, such as the chemical yield, is important and may not be identical at all laboratories. The most common approach to this calculation uses the measured value and ignores the variability of the quantity. For example, if the chemical yield routinely varies between 0.85 and 0.95, but for a particular analysis the yield happens to be 0.928, the MDC for that analysis would be calculated using the value 0.928 with no consideration of the typical range of yields. A consequence of this approach is that the MDC varies randomly when the measurement is repeated under similar conditions; or, in other words, the sample-specific MDC with this approach is a random variable. An MDC calculated in this manner may or may not be useful as a predictor of the future performance of the measurement process.

If sample-specific MDCs are reported, it must be clear that no measured value should ever be compared to an MDC to make a detection decision. In certain cases it may be valid to compare the sample-specific MDC to a required detection limit to determine whether the laboratory has met contractual or regulatory requirements (remembering to consider the uncertainty of the MDC estimate), and in general it may be informative to both laboratory personnel and data users to compare sample-specific MDCs to nominal estimates, but other valid uses for the sample-specific MDC are rare.

20.2.5 The MARLAP Approach to Critical Values and Detection Limits

Historically, detection in radiochemistry has often been based on the distribution of the instrument signal obtained by counting analyte-free *sources*; however, in principle it should be based on the distribution obtained when analyte-free *samples* are analyzed, which is often affected by the processing of samples before instrumental analysis. There is more than one valid approach for dealing with the effects of sample processing. One approach, which is recommended by IUPAC (1995), makes the detection decision for a sample using the critical concentration, x_C, which is calculated on the basis of the distribution of the measured analyte concentration, $\hat{x}$, under the null hypothesis of zero true concentration in the sample. Similarly, the IUPAC approach determines the MDC on the basis of the distribution of $\hat{x}$ as a function of the true concentration.

The approach of this chapter makes detection decisions using the critical net signal, S_C, which is calculated on the basis of the distribution of the net signal, $\hat{S}$, under the same null hypothesis (zero true concentration in the sample). This approach requires one to consider all sources of variability in the signal, including any due to sample processing. So, for example, if the presence of analyte in the reagents causes varying levels of contamination in the prepared sources, this variability may increase the variance of the blank signal and thereby increase the critical net signal.

The MARLAP approach to detection decisions ignores the variability of any term or factor in the measurement model that does not affect the distribution of the instrument signal obtained from samples and blanks. For example, measurement errors in the counting efficiency may increase the variability of the measured concentration, but since they have no effect on the distribution of the signal, they do not affect the critical value, S_C.

The MARLAP approach to the calculation of the MDC also takes into account all sources of variability in the signal, including those related to sample processing, but it ignores any additional sources of variability in the measured concentration that do not affect the distribution of the signal. For example, variability in the true yield from one measurement to another affects the distribution of $\hat{S}$ and thereby increases the MDC, but measurement error in the estimated yield typically does not. The estimated yield is applied as a correction factor to $\hat{S}$; so, errors in its measurement contribute to the variability of the calculated concentration but do not affect the variability of $\hat{S}$ or the true value of the MDC. (On the other hand, yield measurement errors may

make precise determination of the MDC more difficult because they make it harder to determine the distribution of yields.)

20.2.6 Other Detection Terminologies

Another term frequently used for a measure of detection capability is the "lower limit of detection," or LLD (Altshuler, 1963; EPA, 1980; NRC, 1984). Unfortunately this term has been used with more than one meaning. In *Upgrading Environmental Radiation Data* (EPA, 1980), the LLD is defined as a measure of the detection capability of an instrument and is expressed as an activity. However, the Nuclear Regulatory Commission defines the LLD to be identical to the MDC when $\alpha = \beta = 0.05$ (see, for example, NUREG/CR-4007). It is thus a measure of the detection capability of a measurement process and is expressed as an activity *concentration*.

The term "detection limit" is often used as a synonym for "minimum detectable concentration" or for "minimum detectable value" of any other measured quantity.

Many other terms have been used to describe detection capabilities of measurement procedures. Most of them will not be listed here, but one term deserves attention because of the possibility of its confusion with the MDC. The *method detection limit*, or MDL, is a measure of detection capability used routinely in the context of analyzing samples for chemical contaminants.

The term "method detection limit" is defined in the Code of Federal Regulations. In Title 40 CFR Part 136, Appendix B, the following definition appears:

> The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

The definition is later clarified somewhat by a statement that the MDL "is used to judge the significance of a single measurement of a future sample." Thus, the MDL serves as a critical value; however, it is also used as a measure of detection capability, like an MDC. Note that, in MARLAP's usage, the "method detection limit" is not truly a detection limit.

In March 2003, the Federal Register published a proposed revision of the definition of MDL, which would make it clear that the MDL serves as a critical value. The proposed new definition is:

> The method detection limit (MDL) is an estimate of the measured concentration at which there is 99 % confidence that a given analyte is present in a given sample matrix. The MDL is the concentration at which a decision is made regarding

> whether an analyte is detected by a given analytical method. The MDL is calculated from replicate analyses of a matrix containing the analyte and is functionally analogous to the "critical value" described by Currie (1968, 1995 [IUPAC, 1995]) and the Limit of Detection (LOD) described by the American Chemical Society (Keith et al, 1980, McDougal et al., 1983).

At the time of this writing, the proposed revision had not been approved.

The similarity between the abbreviations MDC and MDL tends to produce confusion. The term "method detection limit" is seldom used in the context of radiochemistry except when the analytical method is one that is commonly used to measure stable elements (e.g., ICP-MS methods), or when the term is misused by those who are more familiar with the terminology of hazardous chemical analysis. The confusion is made worse by the fact that "MDL" is sometimes interpreted by radiochemists as an abbreviation for nonstandard terms such as "minimum detectable level" and "minimum detectable limit," the use of which MARLAP strongly discourages.

20.2.7 The Minimum Quantifiable Concentration

The *minimum quantifiable concentration*, or the *minimum quantifiable value* of the analyte concentration, is defined as the concentration of analyte in a laboratory sample at which the measurement process gives results with a specified relative standard deviation.[3] A relative standard deviation of 10 % is usually specified, although other values are possible (see for example MARLAP Appendix C). Since ISO 11843 addresses detection capability but not quantification capability, MARLAP follows IUPAC guidance in defining "minimum quantifiable value" (IUPAC, 1995). IUPAC defines both the minimum quantifiable instrument signal and the minimum quantifiable concentration, although MARLAP considers only the latter. In this document the minimum quantifiable concentration will be abbreviated as MQC and denoted in equations by x_Q.

The term "quantification limit" may be used as a synonym for "minimum quantifiable concentration" or for "minimum quantifiable value" of any other measured quantity.

Section 20.4.3 provides more information about the calculation of the minimum quantifiable concentration.

Historically much attention has been given to the detection capabilities of radiochemical measurement processes, but less attention has been given to quantification capabilities, although for some analytical projects, quantification capability may be a more relevant issue. For example, suppose the purpose of a project is to determine whether the ^{226}Ra concentration in soil from a

[3] The MQC is defined in terms of the relative standard *deviation* of the estimator — not the relative standard *uncertainty* of the measured result. The standard uncertainty is generally an estimate of the standard deviation.

site is below an action level. Since ^{226}Ra occurs naturally in almost any type of soil, the analyte may be assumed to be present in every sample, making detection decisions irrelevant. The MDC of the measurement process obviously should be less than the action level, but a more important question is whether the MQC is less than the action level (see also Chapter 3 and Appendix C).

20.3 Recommendations

MARLAP makes the following recommendations.

- When an analyte detection decision is required, it should be made by comparing the gross signal, net signal, or measured analyte concentration to its corresponding critical value.

- The laboratory should choose expressions for the critical value and minimum detectable value that are appropriate for the structure and statistics of the measurement process. The client may specify the desired Type I and Type II error rates (both 5 % by default) but should not require particular equations for the critical value or the minimum detectable value without detailed knowledge of the measurement process.

- The laboratory should use an appropriate radiochemical blank to predict the signal produced by a sample that contains no analyte. The most appropriate type of blank for this purpose depends on the analyte and on the method and conditions of measurement. Depending on the circumstances, it may be a blank source, reagent blank, or other process blank that accounts for instrument background as well as any contaminants introduced during the processing of the sample.

- The laboratory should confirm the validity of the Poisson approximation for the measurement process before using an expression for the critical value that is based on Poisson statistics. When the analyte is present at observable levels in the water, reagents, and lab ware used in the analysis, the Poisson approximation is often inappropriate. In these cases replicated blanks may be used to determine the critical value.

- The laboratory should consider all sources of variance in the instrument signal (or other response variable) when calculating the critical value and minimum detectable value.

- The minimum detectable value (MDC or MDA) should be used only as a performance characteristic of the measurement process.

- A measurement result should never be compared to the minimum detectable value to make a detection decision.

- The laboratory should report each measurement result and its uncertainty as obtained (as recommended in Chapter 19) even if the result is less than zero. The laboratory should never report a result as "less than MDC."

- The minimum detectable value should not be used for projects where the issue is quantification of the analyte and not detection. For these projects, MARLAP recommends the minimum quantifiable value as a more relevant performance characteristic of the measurement process.

MARLAP neither encourages nor discourages the reporting of sample-specific MDCs with measurement results, so long as the recommendations stated above are followed.

20.4 Calculation of Detection and Quantification Limits

20.4.1 Calculation of the Critical Value

In Section 20.2.2, the *critical value* of the response variable (or gross instrument signal), denoted by y_C, was defined as the response threshold used to decide whether the analyte concentration of a laboratory sample is greater than that of the blank. The critical value of the net instrument signal, denoted by S_C, was similarly defined as the net signal threshold that may be used for the same purpose.

The critical value of the net signal, S_C, is defined symbolically by the relation

$$\Pr[\hat{S} > S_C \mid X = 0] = \alpha \tag{20.1}$$

where $\Pr[\hat{S} > S_C \mid X = 0]$ denotes the probability that the observed net signal, $\hat{S}$, exceeds its critical value, S_C, when the true analyte concentration, X, is zero, and α denotes the significance level, or the specified probability of a Type I error. When the signal assumes only discrete values (e.g., numbers of counts), there may be no value S_C that satisfies Equation 20.1 exactly. The critical value in this case is defined as the smallest value, S_C, such that $\Pr[\hat{S} > S_C \mid X = 0] \leq \alpha$.

Determining a value of S_C which satisfies the definition requires knowledge of the distribution of the net signal, $\hat{S}$, under the assumption that the analyte concentration in the laboratory sample is zero (the null hypothesis). The measured net signal may be written as $\hat{S} = \hat{Y} - \hat{B}$, where $\hat{Y}$ denotes the measured gross signal and $\hat{B}$ denotes the estimated value of the gross signal under the null hypothesis H_0. In the absence of interferences, the value of $\hat{B}$ is usually estimated by measuring one or more blanks using the same procedure used to measure the test sample, and the distribution of $\hat{Y}$ under H_0 is determined from that of $\hat{B}$. In other cases, however, the value of $\hat{B}$ includes estimated baseline and other interferences that are present only during the measurement of the sample and cannot be determined from the blank.

Since S_C, not y_C, has traditionally been used for analyte detection decisions in radiochemistry, the following presentation focuses primarily on S_C. However, conversion of either of these values to the other is simple, because $y_C = S_C + \hat{B}$.

20.4.1.1 Normally Distributed Signals

If the distribution of the net signal $\hat{S}$ under H_0 is approximately normal with a well-known standard deviation, σ_0, the critical value of $\hat{S}$ is

$$S_C = z_{1-\alpha}\sigma_0 \tag{20.2}$$

where $z_{1-\alpha}$ denotes the $(1 - \alpha)$-quantile of the standard normal distribution. Table G.1 in Appendix G shows that $z_{1-\alpha} \approx 1.645$ when $\alpha = 0.05$. Attachment 20A describes the calculation of S_C when the standard deviation is not well-known.

The blank signal, $\hat{B}$, and its standard deviation, σ_B, may be estimated by replicate blank measurements, but at least 20 measurements are generally needed to ensure that the experimental standard deviation, s_B, is an accurate estimate of σ_B. (If fewer than 20 measurements are made, see Attachment 20A.) Given σ_B, the standard deviation, σ_0, of the net signal, $\hat{S} = \hat{Y} - \hat{B}$, under the null hypothesis is equal to

$$\sigma_0 = \sigma_B\sqrt{1 + \frac{1}{n}} \tag{20.3}$$

where n denotes the number of replicate blank measurements. So, the critical net signal is given by

$$S_C = z_{1-\alpha}\sigma_B\sqrt{1 + \frac{1}{n}} \tag{20.4}$$

The preceding equation is valid only if the blank measurements are made in the same manner and under the same conditions as the sample measurement. In particular, count times should be identical for the sample and the blanks.

20.4.1.2 Poisson Counting

Radionuclide analyses typically involve radiation counting measurements. Although radiation counting data never follow the Poisson model exactly, the model may be a useful approximation in some situations, especially those where the mean blank count is extremely low and the observed count therefore does not follow a normal distribution. At somewhat higher count levels, features from both models are often used, since the Poisson distribution may be approximated by a normal distribution. In this case the Poisson model allows one to estimate σ_0 without replication, because one blank measurement provides an estimate of σ_B.

Generally the pure Poisson model is inappropriate when one analyzes for radionuclides that are found in observable quantities in the water, reagents, and lab ware used in the analysis. Some radionuclides, such as the naturally occurring isotopes of uranium, thorium, and radium, may be present as interfering contaminants in the laboratory and require blank corrections that account for their presence and variability in prepared sources. The variability of these contaminant levels usually must be determined by replicate measurements. If variability is found, one may either abandon the Poisson model (in this case see Section 20.4.1.1) or modify it by including additional non-Poisson variance terms (as shown in the next subsection, "The Poisson-Normal Approximation," and in Section 19.5.4 of Chapter 19).

When a test source is analyzed in a radiation counting measurement, either the gross count or the gross count rate may be considered the instrument signal $\hat{Y}$. In this section, it is assumed that the instrument signal is the gross count. Therefore, if there are no interferences, the estimated gross and blank signals are

$$\hat{Y} = N_S \qquad \text{and} \qquad \hat{B} = N_B \frac{t_S}{t_B} \tag{20.5}$$

where

N_S is the gross count (source count);
N_B is the blank count;
t_S is the count time for the test source; and
t_B is the count time for the blank.

If there are interferences, the blank signal is

$$\hat{B} = \left(\frac{N_B}{t_B} + \hat{R}_I \right) t_S \tag{20.6}$$

where $\hat{R}_I$ denotes the estimated count rate due to the interferences. In either case the net instrument signal is the *net count*, defined as $\hat{S} = N_S - \hat{B}$. The net signal is always assumed to have zero mean when analyte-free samples are analyzed.

THE POISSON-NORMAL APPROXIMATION

Suppose the distribution of the blank signal can be estimated using the Poisson model, possibly with an additional small non-Poisson variance component and perhaps a correction for known interferences, and the instrument background remains at a level where the Poisson distribution is approximately normal. Then the critical net count is given approximately by the equation

$$S_C = z_{1-\alpha} t_S \sqrt{\frac{R_B + R_I}{t_S} + \frac{R_B}{t_B} + \xi_B^2 + \sigma^2(\hat{R}_I)} \tag{20.7}$$

where

R_B is the (true) mean count rate of the blank;
R_I is the mean interference count rate;
ξ_B^2 is the non-Poisson variance in the blank (count rate) correction (see Section 19.5.4 of Chapter 19); and
$\sigma^2(\hat{R}_I)$ is the variance of the estimator for R_I.

When there are no interferences and no non-Poisson blank variance, Equation 20.7 becomes

$$S_C = z_{1-\alpha} \sqrt{R_B t_S \left(1 + \frac{t_S}{t_B}\right)} \tag{20.8}$$

The preceding formula is equivalent to "Currie's equation" $L_C = 2.33\sqrt{\mu_B}$ when $t_B = t_S$, $\alpha = 0.05$, and the symbols L_C and μ_B are identified with S_C and $R_B t_S$, respectively (Currie, 1968).

In Equation 20.8, R_B denotes the *true* mean blank count rate, which can only be estimated. In practice one must substitute an estimated value, $\hat{R}_B$, for R_B, as shown in the following equation.

$$S_C = z_{1-\alpha} \sqrt{\hat{R}_B t_S \left(1 + \frac{t_S}{t_B}\right)} \tag{20.9}$$

Equation 20.9 resembles Equation 20.8 but involves the estimated count rate, $\hat{R}_B$, which varies with repeated measurements. The value of $\hat{R}_B$ is usually estimated from the same blank value N_B used to calculate the net instrument signal. (See Attachment 20A for other possible estimators.)

$$\hat{R}_B = \frac{N_B}{t_B} \tag{20.10}$$

The resulting formula, shown below, is equivalent to equations published by several authors (Currie, 1968; Lochamy, 1976; Strom and Stansbury, 1992; ANSI N13.30).

$$S_C = z_{1-\alpha} \sqrt{N_B \frac{t_S}{t_B} \left(1 + \frac{t_S}{t_B}\right)} \tag{20.11}$$

Note that this is a commonly used expression for the critical net count, but its validity depends on the assumption of pure Poisson counting statistics. If the variance of the blank signal is affected by sample processing, interferences, or background instability, then Equation 20.11 may be invalid (but Equation 20.7 may be appropriate).

If $\alpha = 0.05$ and $t_B = t_S$, Equation 20.11 leads to the well-known expression $2.33\sqrt{N_B}$ for the critical net count.

When the blank count is high (e.g., 100 or more), Equation 20.11 works well. At lower blank levels, it can produce a high rate of Type I errors. For example, if the true mean blank count is 0.693, there is a 25 % chance of observing 0 blank counts and a positive number of test source counts in paired measurements of equal duration. In this case, a critical value calculated by Equation 20.11 produces Type I errors more than 25 % of the time regardless of the chosen significance level α. Attachment 20A describes several expressions for S_C that have been proposed for use in situations where the mean blank count is less than 100.

EXAMPLE 20.1

Problem: A 6000-second blank measurement is performed on a proportional counter and 108 beta counts are observed. A test source is to be counted for 3000 s. Estimate the critical value of the net count when $\alpha = 0.05$. (See also Example 20.10.)

Solution:

$$S_C = z_{1-\alpha}\sqrt{N_B \frac{t_S}{t_B}\left(1 + \frac{t_S}{t_B}\right)}$$

$$= 1.645\sqrt{108\left(\frac{3000\text{ s}}{6000\text{ s}}\right)\left(1 + \frac{3000\text{ s}}{6000\text{ s}}\right)}$$

$$= 14.8 \text{ net counts.}$$

EXAMPLE 20.2

Problem: Repeat the same problem assuming the blank correction, expressed as a count rate, has a non-Poisson uncertainty component of $\xi_B = 0.001\ s^{-1}$ (see Section 19.5.4 of Chapter 19).

Solution:

$$S_C = z_{1-\alpha}\sqrt{N_B \frac{t_S}{t_B}\left(1 + \frac{t_S}{t_B}\right) + \xi_B^2 t_S^2}$$

$$= 1.645\sqrt{108\left(\frac{3000\text{ s}}{6000\text{ s}}\right)\left(1 + \frac{3000\text{ s}}{6000\text{ s}}\right) + (0.001\text{ s}^{-1})^2(3000\text{ s})^2}$$

$$= 15.6 \text{ net counts.}$$

20.4.1.3 Batch Blanks

Equation 20.11 is derived with the assumption that a detection decision is based on counts obtained from a single radiation counter. When laboratory samples are analyzed in batches, it is common to analyze a single blank per batch, so that the measurement conditions for the blank may differ somewhat from those of the samples. In particular, the counts for the laboratory samples and the blank may be measured using different detectors. If detection in a laboratory sample is defined relative to a blank counted on a different instrument, Equation 20.11 is inappropriate. Even if a single instrument is used, the presence of positive amounts of analyte in the reagents probably invalidates the (pure) Poisson assumption. In principle, $\hat{B}$ should be estimated by converting the absolute activity of the blank Z_B to an estimated gross count on the instrument used to measure the laboratory sample. Thus,

$$\hat{B} = F(Z_B) \tag{20.12}$$

where

F is the calibration function for the laboratory sample measurement, whose parameters include the instrument background, counting efficiency, chemical yield, and any estimated interferences and

Z_B is the estimated absolute activity of the blank.

Then the net count is $\hat{S} = \hat{Y} - \hat{B}$, whose critical value is

$$S_C = z_{1-\alpha}\sqrt{\sigma^2(\hat{Y}_0) + \sigma^2(\hat{B})} \tag{20.13}$$

where

$\sigma^2(\hat{Y}_0)$ is the variance of the gross count $\hat{Y}$ in the test source measurement when the sample is analyte-free and

$\sigma^2(\hat{B})$ is the variance of the estimator $\hat{B}$.

If Poisson counting statistics are assumed, then $\sigma^2(\hat{Y}_0)$ may be estimated by $\hat{B}$ (assuming $\hat{B} > 0$), but estimating $\sigma^2(\hat{B})$ still requires a more complicated expression, which may be based on uncer-

tainty propagation or replication. The variance of $\hat{B}$ may be difficult to estimate if positive blank values are caused not by the presence of the analyte in reagents but by contaminated glassware or instruments, which may represent a loss of statistical control of the analytical process.

A valid alternative to the approach just described is to use replicate blank measurements to determine the distribution of the measured total activity and to calculate the critical net (absolute) activity using an equation similar to Equation 20.4. The critical net activity is given by

$$Critical\ Net\ Activity = z_{1-\alpha}\sigma_{\text{blank}}\sqrt{1+\frac{1}{n}} \tag{20.14}$$

where σ_{blank} denotes the standard deviation of the blank activity and n denotes the number of replicate blank measurements. Then a detection decision is made for a real sample by comparing the measured net activity to the critical net activity.

This approach should work best if all samples and blanks are analyzed under very similar conditions, using instruments with similar counting efficiencies and background levels. (Each sample result and each blank result must still be corrected for instrument background.) If the instruments are significantly different, special care may be needed to ensure that the replicate blank measurements are made using all the available instruments and that samples are assigned to instruments randomly so that the variance of the blank results is similar to the variance observed when analyte-free samples are analyzed.

20.4.2 Calculation of the Minimum Detectable Concentration

The *minimum detectable concentration* (MDC) is defined as the concentration of analyte x_D that must be present in a laboratory sample to give a specified probability, $1 - \beta$, of obtaining a measured response greater than its critical value, leading one to conclude correctly that there is analyte in the sample. In other words, the MDC is the analyte concentration at which the type II error rate is β.

The MDC may also be defined as the analyte concentration x_D that satisfies the relation

$$\Pr[\hat{S} \le S_C \mid X = x_D] = \beta \tag{20.15}$$

where the expression $\Pr[\hat{S} \le S_C \mid X = x_D]$ is read as "the probability that the net signal $\hat{S}$ does not exceed its critical value S_C when the true concentration X is equal to x_D."

The MDC is often used as a performance measure for an analytical process for the purpose of comparing different analytical procedures or evaluating a laboratory's capabilities against specified requirements. The calculation of the "nominal" MDC is complicated by the fact that some

input quantities in the mathematical model, such as interferences and the chemical yield, which have a substantial impact on the MDC, may vary significantly from measurement to measurement. Other quantities that may have similar effects include the decay time, counting efficiency, and instrument background. Because of these variable quantities, determining the value of x_D that satisfies Equation 20.15 in practice may be difficult. One common approach to this problem is to make conservative choices for the values of the variable quantities, which tend to increase the value of x_D.

The MDC is also commonly used in radiochemistry to describe the detection capability of the analytical process as implemented in a particular instance. In this case, the need for conservative choices is reduced. Instead, the measured values of the variable quantities may be used. However, since the measured values have uncertainties, their uncertainties contribute to a combined standard uncertainty in the calculated value of x_D. To ensure compliance with regulatory or contractual requirements, an uncertainty interval or conservative upper bound for x_D may still be useful (see NRC, 1984).

20.4.2.1 The Minimum Detectable Net Instrument Signal

The traditional method for calculating the MDC involves first calculating the *minimum detectable value of the net instrument signal* and then converting the result to a concentration using the mathematical measurement model. The minimum detectable value of the net instrument signal, denoted by S_D, is defined as the mean value of the net signal that gives a specified probability, $1 - \beta$, of yielding an observed signal greater than its critical value S_C. Thus,

$$\Pr[\hat{S} \le S_C \mid S = S_D] = \beta \tag{20.16}$$

where S denotes the true mean net signal.

In radiochemistry the mean net signal, S, is usually directly proportional to X, the true analyte concentration in the sample. So, there is a "sensitivity" constant, A, such that $S = AX$. The constant A typically is the mean value of the product of factors such as the source count time, decay-correction factor, yield, counting efficiency, and test portion size (e.g., mass or volume). Its value in some cases may be sample-dependent, but it is essentially independent of the analyte concentration over a wide range of values. Combining Equation 20.16 with the relation $S = AX$ gives

$$\Pr[\hat{S} \le S_C \mid X = S_D / A] = \beta \tag{20.17}$$

A comparison of Equation 20.17 to Equation 20.15, the defining relation of the minimum detectable concentration, x_D, shows that

$$x_D = \frac{S_D}{A} \tag{20.18}$$

The preceding equation is only true if all sources of variability are accounted for when determining the distribution of the net signal, $\hat{S}$. If sample-processing effects are ignored, the expression S_D / A may underestimate the MDC. Note that ensuring the MDC is not underestimated also requires that the value of A not be overestimated.

Certain variations of this procedure for calculating S_D and x_D may also be useful. As an example, suppose

$$A = t_S \mu_Y \mu_V \mu_\varepsilon \mu_D \mu_{F_S} \tag{20.19}$$

where

t_S	the source count time;
μ_Y	the mean chemical yield;
μ_V	the mean test portion size (mass or volume);
μ_ε	the mean counting efficiency;
μ_D	the mean decay-correction factor; and
μ_{F_S}	the mean "subsampling factor," defined in Chapter 19 as the ratio of analyte concentration in a subsample to that in a sample (μ_{F_S} is assumed to be 1).

Much of the guidance given later for calculating S_D presumes that the distribution of the signal is normal, but the distribution tends not to be normal if the true yield (Y), test portion size (V), counting efficiency (ε), decay-correction factor (D), or subsampling factor (F_S) is not normally distributed, or if the total relative variance of the product of these factors is large. For example, suppose the yield and decay factor vary over large ranges and are not normally distributed but the other factors are either constant or approximately normal. Then a reasonable method of calculating x_D is to ignore the variances of Y and D when calculating S_D but to compensate for their omission by replacing $\mu_Y \mu_D$ in the expression for the sensitivity factor, A, by a lower value, such as the β-quantile of the historical distribution of YD (i.e., the 5th percentile when $\beta = 0.05$). In general, the variance of any or all of the factors may be ignored if a sufficiently conservative value is substituted for the mean value of the product of those factors when estimating the sensitivity factor, A.

20.4.2.2 Normally Distributed Signals

If the net signal, $\hat{S}$, is normally distributed and its estimated standard deviation, σ_0, under H_0 is well-known, the critical value of $\hat{S}$ is $S_C = z_{1-\alpha}\sigma_0$, as previously noted. Then the minimum detectable net signal, S_D, is determined implicitly by the equation

$$S_D = S_C + z_{1-\beta}\sqrt{\sigma^2(\hat{S} \mid S = S_D)} \tag{20.20}$$

where $\sigma^2(\hat{S} \mid S = S_D)$ denotes the variance of the measured signal, $\hat{S}$, when the true mean signal, S, equals S_D. If the function $\sigma^2(\hat{S} \mid S = S_D)$ is constant, Equation 20.20 gives the value of S_D immediately, but typically $\sigma^2(\hat{S} \mid S = S_D)$ is an increasing function of S_D.

If the function $\sigma^2(\hat{S} \mid S = S_D)$ has a simple form, it may be possible to transform Equation 20.20 by algebraic manipulation into an explicit formula for S_D. For example, the variance of $\hat{S}$ often has the form

$$\sigma^2(\hat{S}) = aS^2 + bS + c \tag{20.21}$$

where S denotes the true mean net signal and the constants a, b, and c do not depend on S (see Section 20.4.2.3, "Poisson Counting"). In this case the minimum detectable net signal is given by

$$S_D = \frac{1}{I_\beta}\left(S_C + \frac{z_{1-\beta}^2 b}{2} + z_{1-\beta}\sqrt{bS_C + \frac{z_{1-\beta}^2 b^2}{4} + aS_C^2 + I_\beta c} \right) \tag{20.22}$$

where $I_\beta = 1 - z_{1-\beta}^2 a$. When $\alpha = \beta$, the preceding equation can be simplified to the following.

$$S_D = \frac{bz_{1-\beta}^2 + 2S_C}{1 - z_{1-\beta}^2 a} \tag{20.23}$$

In Equations 20.21 and 20.22, the constant c equals σ_0^2, the variance of the net signal, $\hat{S}$, when analyte-free samples are analyzed. If Poisson counting statistics are assumed (possibly with other sources of variance) and the signal S is the net count, as defined earlier, the constant b usually equals 1. In some situations, such as alpha-counting ^{222}Rn and its short-lived progeny in an alpha scintillation cell, a different value of b may be needed because of the different counting statistics.[4]

For typical radiochemistry measurement models, the value of the constant a is the relative variance (squared coefficient of variation) of the overall sensitivity, which is the product of factors such as the count time, yield, counting efficiency, and subsampling factor. In general the relative variance of a product of independent positive factors $F_1, F_2, \ldots, F_N$ is given by

$$\varphi^2(F_1 F_2 \cdots F_N) = (1 + \varphi^2(F_1))(1 + \varphi^2(F_2)) \cdots (1 + \varphi^2(F_N)) - 1 \tag{20.24}$$

where φ^2 denotes relative variance, although an adequate approximation is usually given by

[4] Note that b equals the "index of dispersion" of the counts produced by net sample activity (the ratio of the variance to the mean). See Lucas and Woodward (1964) for more information about the counting statistics of alpha-scintillation cells.

$$\varphi^2(F_1 F_2 \cdots F_N) \approx \varphi^2(F_1) + \varphi^2(F_2) + \cdots + \varphi^2(F_N) \tag{20.25}$$

when each coefficient of variation, $\varphi(F_i)$, is small. So, if the coefficients of variation of the yield, counting efficiency, subsampling factor, and other such factors are known, the value of a can be calculated.

EXAMPLE 20.3

Problem: Suppose the sensitivity is the product of the yield (Y), counting efficiency (ε), test portion size (V), count time (t_S), and subsampling factor (F_S), and that essentially all of the variance of this product is generated by the variances of the yield and subsampling factor. Assume the coefficients of variation of these two factors are

$\varphi(Y) = 0.06$
$\varphi(F_S) = 0.03$

Assume the counts produced by the net sample activity follow Poisson counting statistics, and assume that σ_0^2, the variance of the net count observed when analyte-free samples are analyzed, equals 209. Determine the values of the constants a, b, and c such that $\sigma^2(\hat{S}) = aS^2 + bS + c$.

Solution: The value of a is determined using Equation 20.24, as follows:

$$\begin{aligned} a = \varphi^2(YF_S) &= (1 + \varphi^2(Y))(1 + \varphi^2(F_S)) - 1 \\ &= (1 + 0.06^2)(1 + 0.03^2) - 1 \\ &= 0.0045 \end{aligned}$$

The value of b is 1, because Poisson counting statistics are assumed. The value of c equals σ_0^2, or 209. So, the variance of the net signal, $\hat{S}$, is given by the equation

$$\sigma^2(\hat{S}) = (0.0045 \times S^2) + S + 209$$

ITERATIVE METHODS

If Equation 20.20 cannot be transformed algebraically, an iterative procedure, such as fixed-point iteration, may be used to solve the equation for S_D. An outline of fixed-point iteration is shown below.[5]

[5] Fixed-point iteration, or functional iteration, is the term for a general technique for solving an equation of the form $x = f(x)$. The iteration produces a sequence $x_0, x_1, x_2, \ldots$, where $x_{n+1} = f(x_n)$. Under certain conditions, the sequence converges to a fixed point of f, where $f(x) = x$. Newton's Method for finding a zero of a function $g(x)$ is one example

1. Initially calculate $S_D = S_C + z_{1-\beta}\sqrt{\sigma^2(\hat{S} \mid S = S_C)}$ (using $S = S_C$)
2. **repeat loop (Lines 3–4)**
3. Set $h = S_D$
4. Recalculate $S_D = S_C + z_{1-\beta}\sqrt{\sigma^2(\hat{S} \mid S = h)}$ (using $S = h$)
5. **until** $|S_D - h|$ is sufficiently small
6. **output** the solution S_D

In many cases, one iteration of the loop (Lines 3–4) provides an adequate approximation of S_D. In almost all cases, repeated iteration produces an increasing sequence of approximations converging upward to the solution; so, the stopping condition at Line 5 may be replaced by "**until** $S_D \le h$" to obtain full machine precision in the result.

EXAMPLE 20.4

Problem: Assume the variance of the net signal, $\hat{S}$, is given by

$$\sigma^2(\hat{S}) = (0.0045 \times S^2) + S + 209$$

where 0.0045 is the value of the constant a determined in Example 20.3, assuming a 3 % coefficient of variation in the subsampling factor and a 6 % coefficient of variation in the yield. Let $\alpha = \beta = 0.05$. The critical net signal, S_C, is calculated as follows.

$$S_C = z_{1-\alpha}\sqrt{\sigma^2(\hat{S} \mid S = 0)} = 1.645\sqrt{209} = 23.78$$

Use fixed-point iteration to calculate S_D.

Solution: The algorithm produces a sequence of approximations.

$$S_{D,0} = 23.78 + 1.645\sqrt{\sigma^2(\hat{S} \mid S = 23.78)} = 49.02$$
$$S_{D,1} = 23.78 + 1.645\sqrt{\sigma^2(\hat{S} \mid S = 49.02)} = 50.75$$
$$S_{D,2} = 23.78 + 1.645\sqrt{\sigma^2(\hat{S} \mid S = 50.75)} = 50.88$$

of the technique.

$$S_{D,3} = 23.78 + 1.645\sqrt{\sigma^2(\hat{S} \mid S = 50.88)} = 50.89$$

$$S_{D,4} = 23.78 + 1.645\sqrt{\sigma^2(\hat{S} \mid S = 50.89)} = 50.89$$

The sequence converges to 50.89, which is the value of S_D.

Notice that the same value can be calculated using Equation 20.22 or 20.23 with the constants $a = 0.0045$, $b = 1$, $c = 209$.

20.4.2.3 Poisson Counting

If the following assumptions are true:

- The mean blank count is at least 100
- The only source of signal variance considered is Poisson counting statistics
- $\alpha = \beta$
- Equation 20.11 is used to calculate the critical net signal, S_C

then the minimum detectable net signal, S_D, is given by the following simple equation.[6]

$$S_D = z^2_{1-\beta} + 2S_C \tag{20.26}$$

In the special case when $\alpha = \beta = 0.05$, Equation 20.26 becomes

$$S_D = 2.71 + 2S_C \tag{20.27}$$

In the case when $\alpha \neq \beta$, S_D is determined from Equation 20.22 using the following values for a, b, and c.

$$a = 0 \qquad b = 1 \qquad c = R_B t_S \left(1 + \frac{t_S}{t_B} \right)$$

The resulting formula for S_D is

[6] Some references use the value 3 instead of $z^2_{1-\beta}$ in this formula. A straightforward derivation gives the value $z^2_{1-\beta}$, which is approximately 2.71 when $\beta = 0.05$, but replacing this value by $-\ln \beta$ (approximately 3 when $\beta = 0.05$) accounts for the fact that when the mean count is low, a Poisson distribution is only imperfectly approximated by a normal distribution. The value $-\ln \beta$ is the exact value of S_D when the mean blank count rate is zero, because in this case $S_C = 0$, and $\Pr[\hat{S} = 0] \leq \beta$ if and only if $S \geq -\ln \beta$. Note also that the equation in the text is valid only if $\alpha = \beta$. MARLAP considers either $z^2_{1-\beta}$ or $-\ln \beta$ to be an acceptable value in this case.

$$S_D = S_C + \frac{z_{1-\beta}^2}{2} + z_{1-\beta}\sqrt{\frac{z_{1-\beta}^2}{4} + S_C + R_B t_S\left(1 + \frac{t_S}{t_B}\right)} \qquad (20.28)$$

EXAMPLE 20.5

Problem: Consider Example 20.1 again, where a 6000-second blank measurement on a proportional counter produces 108 beta counts and a test source is to be counted for 3000 s. Assume this blank measurement gives the best available estimate of the true mean blank count rate, R_B, and use Equation 20.27 to calculated the minimum detectable net signal, S_D, using the default value, 0.05, for Type I and Type II error probabilities. Also use Equation 20.28 to calculate S_D for $\alpha = 0.05$ and $\beta = 0.10$.

Solution: As in Example 20.1, the critical net count, S_C, equals 14.8. The count times are t_S = 3000 s and t_B = 6000 s. The mean blank count rate, R_B, is estimated by

$$R_B \approx \frac{108}{6000\ \text{s}} = 0.018\ \text{s}^{-1}$$

For the first part of the problem, Equation 20.27 may be used, because $\alpha = \beta = 0.05$. It gives the result

$$S_D = 2.71 + 2(14.8) = 32.3\ \text{net counts}$$

For the second part of the problem, Equation 20.28 is used, because $\alpha \neq \beta$.

$$\begin{aligned} S_D &= S_C + \frac{z_{1-\beta}^2}{2} + z_{1-\beta}\sqrt{\frac{z_{1-\beta}^2}{4} + S_C + R_B t_S\left(1 + \frac{t_S}{t_B}\right)} \\ &= 14.8 + \frac{1.282^2}{2} + 1.282\sqrt{\frac{1.282^2}{4} + 14.8 + (0.018\ \text{s}^{-1})(3{,}000\ \text{s})\left(1 + \frac{3000\ \text{s}}{6000\ \text{s}}\right)} \\ &= 28.2\ \text{net counts} \end{aligned}$$

As previously noted, counting data never follow the Poisson model exactly. Variable factors such as the yield, counting efficiency, subsampling error, and source geometry and placement tend to increase a, while interferences and background instability tend to increase c. So, using any of Equations 20.26–28 to calculate S_D is only appropriate if a conservative value of the sensitivity factor, A, (such as the β-quantile of the distribution of the true sensitivity) is used when converting S_D to the MDC. The following example illustrates the calculation of S_D and x_D when both Poisson counting statistics and other sources of variance are considered.

EXAMPLE 20.6

Problem: Again consider the scenario of Example 20.5, where $t_B = 6000$ s, $t_S = 3000$ s, and $R_B \approx 0.018$ s^{-1}. Let the measurement model be

$$X = \frac{N_S - (N_B t_S / t_B)}{t_S \varepsilon Y m_S D F_S}$$

where

X	is the specific activity of the radionuclide in the sample;
ε	is the counting efficiency;
Y	is the yield;
m_S	is the mass of the test portion;
D	is the decay-correction factor (calculated); and
F_S	is the subsampling factor.

Assume:

- the mass of the test portion is always between 0.98 g and 1.05 g
- the half-life of the analyte is 5.07 d, and decay times from collection to start of counting range from about 3 d to about 10 d
- the counting efficiency has mean 0.42 and a 2 % coefficient of variation
- the yield has approximate mean 0.85 and a 5 % coefficient of variation
- the subsampling factor, whose mean is assumed to be 1, has a 3 % coefficient of variation
- background instability contributes a non-Poisson standard deviation of 0.001 s^{-1} to the blank correction, expressed as a count rate (see Section 19.5.4 of Chapter 19).

Calculate S_D and x_D using the value 0.05 for both the Type I and Type II error probabilities.

Solution: First determine how to handle each variable sensitivity factor. The following approach is reasonable.

- The source count time, t_S, has negligible variability; so, use the given value 3000 s and ignore the variance.
- The mass of the test portion, m_S, has only a little variability; so, use the lower bound, 0.98 g, and ignore the variance of m_S.
- The decay-correction factor, D, can vary significantly from sample to sample, but no information is given about the distribution except its range of values. Assume a rectangular distribution of decay times from 3 d to 10 d, and calculate the 95th percentile, $3 + 0.95(10 - 3) = 9.65$ d, which gives the 5th percentile of the decay-correction factor (calculated below).

- Use the stated mean values of the counting efficiency (ε), yield (Y), and subsampling factor (F_S) to calculate the sensitivity factor, and use the stated coefficients of variation for these factors when calculating S_D.

Next write an expression for the variance of the net signal, $\hat{S}$. The Poisson counting variance is given by

$$\text{Poisson variance of}\left(N_S - N_B\frac{t_S}{t_B}\right) = E(N_S) + E(N_B)\frac{t_S^2}{t_B^2} = (S + R_B t_S) + R_B\frac{t_S^2}{t_B}$$

where $E(\cdot)$ denotes expectation. The non-Poisson variance of the background contributes to $\hat{S}$ an additional variance component equal to $(0.001)^2 t_S^2$. The variability of the efficiency, yield, and subsampling factor contribute a variance component of

$$\left((1 + 0.02^2)(1 + 0.05^2)(1 + 0.03^2) - 1\right) \times S^2 = 0.0038 \times S^2$$

Therefore, the total variance of $\hat{S}$ is given by

$$\begin{aligned}\sigma^2(\hat{S}) &= \left(S + R_B t_S\right) + R_B\frac{t_S^2}{t_B} + (0.001\ \text{s}^{-1})^2 t_S^2 + (0.0038 \times S^2) \\ &= (0.0038 \times S^2) + S + R_B t_S\left(1 + \frac{t_S}{t_B}\right) + (0.001\ \text{s}^{-1})^2 t_S^2\end{aligned}$$

So, let a, b, and c be as follows.

$$a = 0.0038 \qquad b = 1 \qquad c = R_B t_S\left(1 + \frac{t_S}{t_B}\right) + (0.001\ \text{s}^{-1})^2 t_S^2 = 90$$

As in Example 20.2, the critical net count, S_C, equals 15.6. Then Equation 20.23 gives the minimum detectable net signal, S_D.

$$S_D = \frac{(1)(1.645)^2 + 2(15.6)}{1 - (1.645)^2(0.0038)} = \frac{33.918}{0.9897} = 34.3 \text{ counts}$$

The value of the sensitivity factor, A, is obtained from the product of the chosen values for the count time, counting efficiency, yield, test portion size, decay factor, and subsampling factor. The decay constant, λ, must be calculated from the half-life, $T_{1/2} = 5.07$ d.

$$\lambda = \frac{\ln 2}{T_{1/2}} = \frac{0.693147}{(5.07\text{ d})(86{,}400\text{ s/d})} = 1.582 \times 10^{-6}\text{ s}^{-1}$$

Then the decay-correction factor is calculated.

$$D = e^{-\lambda t_D}\frac{1 - e^{-\lambda t_S}}{\lambda t_S} = e^{-(1.582\times10^{-6}\text{ s}^{-1})(9.65\text{ d})(86{,}400\text{ s/d})}\frac{1 - e^{-(1.582\times10^{-6}\text{ s}^{-1})(3000\text{ s})}}{(1.582\times10^{-6}\text{ s}^{-1})(3000\text{ s})} = 0.2667$$

So, the sensitivity factor is

$$A = t_S \varepsilon Y m_S D F_S = (3000\text{ s})(0.42)(0.85)(0.98\text{ g})(0.2667)(1) = 279.9\text{ g}\cdot s$$

Therefore, the minimum detectable concentration is

$$x_D = \frac{S_D}{A} = \frac{34.3}{279.9} = 0.12\text{ Bq/g}$$

20.4.2.4 More Conservative Approaches

More conservative (higher) estimates of the MDC may be obtained by following the recommendations of NUREG/CR-4007, in which formulas for MDC (LLD) include estimated bounds for relative systematic error in the blank determination (Δ_B) and the sensitivity (Δ_A). The critical net count S_C is increased by $\Delta_B\hat{B}$, and the minimum detectable net count S_D is increased by $2\Delta_B\hat{B}$. The MDC is then calculated by dividing S_D by the sensitivity and multiplying the result by $1 + \Delta_A$. The NUREG's conservative approach treats random errors and systematic errors differently to ensure that the MDC for a measurement process is unlikely to be consistently underestimated, which is an important consideration if the laboratory is required by regulation or contract to achieve a specified MDC.

20.4.2.5 Experimental Verification of the MDC

To ensure that the MDC has been estimated properly, one may test the estimate experimentally by analyzing n identical control samples spiked with an analyte concentration equal to x_D. If the MDC has been determined properly (the null hypothesis), the probability of failing to detect the analyte in each control sample is at most β. Then the number of nondetectable results in the experiment may be assumed to have a binomial distribution with parameters n and β. If k nondetectable results are actually obtained, one calculates the cumulative binomial probability

$$P = \sum_{j=k}^{n} \binom{n}{j} \beta^j (1-\beta)^{n-j} \quad \text{or} \quad 1 - \sum_{j=0}^{k-1} \binom{n}{j} \beta^j (1-\beta)^{n-j} \tag{20.29}$$

and rejects the null hypothesis if P is smaller than the chosen significance level for the test (which may differ from the significance level for the analyte detection test).

NOTE: For any nonnegative integers n and j, the notation $\binom{n}{j}$ denotes a *binomial coefficient*, usually read "n choose j," which is the number of possible combinations of n objects chosen j at a time. For $0 \le j \le n$, the value of $\binom{n}{j}$ equals $\frac{n!}{j!(n-j)!}$, where the symbol ! denotes the factorial operator. The number of combinations of n objects chosen j at a time is also denoted sometimes by ${}_nC_j$.

To make the test realistic, one should ensure that the physical and chemical characteristics of the control samples, including potential interferences, are representative of laboratory samples encountered in practice.

EXAMPLE 20.7

Problem: Assume x_D is estimated with $\beta = 0.05$. As a check, 10 control samples spiked with concentration x_D are analyzed and 3 of the 10 produce nondetectable results. Does x_D appear to have been underestimated (at the 10 % level of significance)?

Solution: The variables are $n = 10$, $\beta = 0.05$, and $k = 3$. Calculate the P-value

$$P = 1 - \sum_{j=0}^{2} \binom{10}{j} (0.05)^j (0.95)^{10-j} = 1 - 0.9885 = 0.0115$$

Since $P \le 0.10$, reject the null hypothesis and conclude that the MDC was underestimated.

20.4.3 Calculation of the Minimum Quantifiable Concentration

The *minimum quantifiable concentration* (MQC), or the *minimum quantifiable value* of the concentration, was defined in Section 20.2.7 as the analyte concentration in a laboratory sample that gives measured results with a specified relative standard deviation $1 / k_Q$, where k_Q is usually chosen to be 10.

Calculation of the MQC requires that one be able to estimate the standard deviation for the result of a hypothetical measurement performed on a laboratory sample with a specified analyte concentration. Section 19.5.13 of Chapter 19 discusses the procedure for calculating the standard deviation for such a hypothetical measurement.

The MQC is defined symbolically as the value x_Q that satisfies the relation

$$x_Q = k_Q \sqrt{\sigma^2(\hat{X} \mid X = x_Q)} \tag{20.30}$$

where $\sigma^2(\hat{X} \mid X = x_Q)$ denotes the variance of the estimator $\hat{X}$ when the true concentration X equals x_Q. If the function $\sigma^2(\hat{X} \mid X = x_Q)$ has a simple form, it may be possible to solve Equation 20.30 for x_Q using only algebraic manipulation. Otherwise, fixed-point iteration, which was introduced in Section 20.4.2, may be used. The use of fixed-point iteration for this purpose is shown below.

1. Initially calculate $x_Q = k_Q \sqrt{\sigma^2(\hat{X} \mid X = 0)}$ (using $X = 0$)
2. **repeat loop (Lines 3–4)**
3. Set $h = x_Q$
4. Recalculate $x_Q = k_Q \sqrt{\sigma^2(\hat{X} \mid X = h)}$ (using $X = h$)
5. **until** $|x_Q - h|$ is sufficiently small
6. **output** the solution x_Q

The sequence of values generated by the algorithm typically converges upward to the solution.

When Poisson counting statistics are assumed, possibly with excess variance components, and the mathematical model for the analyte concentration is $X = S / A$, where S is the net count, A denotes the overall sensitivity of the measurement, Equation 20.30 may be solved for x_Q to obtain the formula

$$x_Q = \frac{k_Q^2}{2AI_Q}\left(1 + \sqrt{1 + \frac{4I_Q}{k_Q^2}\left(R_B t_S\left(1 + \frac{t_S}{t_B}\right) + \xi_B^2 t_S^2 + R_I t_S + \sigma^2(\hat{R}_I) t_S^2\right)}\right) \tag{20.31}$$

where

t_S is the count time for the test source;
t_B is the count time for the blank;
R_B is the mean blank count rate;
ξ_B^2 is the non-Poisson variance component of the blank count rate correction;
R_I is the mean interference count rate;
$\sigma(\hat{R}_I)$ is the standard deviation of the measured interference count rate;
$\varphi_{\hat{A}}^2$ is the relative variance of the measured sensitivity, $\hat{A}$, including the subsampling variance; and

I_Q is equal to $1 - k_Q^2 \varphi_{\hat{A}}^2$.

If the true sensitivity A may vary, then a conservative value, such as the 0.05-quantile $A_{0.05}$, should be substituted for A in the formula. Note that $\varphi_{\hat{A}}^2$ denotes only the relative variance of $\hat{A}$ due to subsampling and measurement error — it does not include the variance of the true sensitivity, A.

Note that Equation 20.31 defines the MQC only if $I_Q > 0$. If $I_Q \leq 0$, the MQC is infinite, because there is no concentration at which the relative standard deviation of $\hat{X}$ fails to exceed $1 / k_Q$. In particular, if the relative standard deviation of the measured sensitivity $\hat{A}$ or the subsampling standard deviation φ_{Samp} exceeds $1 / k_Q$, then $I_Q < 0$ and the MQC is infinite.

More generally, if the variance of the measured concentration $\hat{X}$ can be expressed in the form $\sigma^2(\hat{X}) = aX^2 + bX + c$, where a, b, and c do not depend on X, then the MQC is given by the formula

$$x_Q = \frac{k_Q^2}{2(1 - k_Q^2 a)} \left(b + \sqrt{b^2 + \frac{4c(1 - k_Q^2 a)}{k_Q^2}} \right) \tag{20.32}$$

For example, if pure Poisson counting statistics are assumed and there are no interferences, then $a = \varphi_{\hat{A}}^2$, $b = 1 / A$, and $c = R_B t_S (1 + t_S / t_B) / A^2$.

EXAMPLE 20.8

Problem: Refer once more to Examples 20.5 and 20.6, where the measurement model is given by

$$X = \frac{N_S - (N_B t_S / t_B)}{t_S \varepsilon Y m_S D F_S}$$

where

X	is the specific activity of the radionuclide in the sample;
N_S	is the sample (gross) count;
N_B	is the blank count;
t_S	is the sample count time (s);
t_B	is the blank count time (s);
ε	is the counting efficiency;
Y	is the yield;
m_S	is the mass of the test portion (g);
D	is the decay-correction factor; and
F_S	is the subsampling factor.

Keep the same assumptions as in the earlier examples. Assume also that the relative standard deviation of the yield measurement (as opposed to that of the yield itself) is 3 %, and that the relative standard deviation of the efficiency measurement is 2 %. Use Equation 20.31 to calculate the minimum quantifiable concentration, x_Q, defined as the analyte concentration at which the relative standard deviation of the measurement process is 10 %.

Solution: The relative measurement variance of the sensitivity, $\varphi^2_{\hat{A}}$, is assumed to be the sum of the relative subsampling variance and the relative measurement variances of Y and ε, since the other sensitivity factors are measured with better relative precision. As in the earlier example, conservative values for m_S (0.98 g) and D (0.2667) will be used in the calculation of the sensitivity factor, A. However, for this problem, a somewhat conservative value of the yield will also be used, because the true yield has a 5 % relative standard deviation, which is not otherwise taken into account. Since the mean value of the yield is 0.85 and the relative standard deviation is 5 %, estimate the 0.05-quantile of the yield as follows:

$$Y = 0.85 \times (1 - 1.645 \times 0.05) = 0.78$$

The following values are also used in this problem.

$$t_S = 3000 \text{ s}$$
$$t_B = 6000 \text{ s}$$
$$R_B = 0.018 \text{ s}^{-1}$$
$$\varepsilon = 0.42$$
$$R_I = 0,\ \sigma^2(\hat{R}_I) = 0,\ \xi_B = 0$$
$$k_Q = 10$$
$$\varphi_\varepsilon = 0.02$$
$$\varphi_Y = 0.03$$
$$\varphi_{Samp} = 0.03$$
$$\varphi^2_{\hat{A}} = \varphi^2_\varepsilon + \varphi^2_Y = \varphi^2_{Samp} = 0.02^2 + 0.03^2 + 0.03^2$$
$$I_Q = 1 - k^2_Q \varphi^2_{\hat{A}} = 1 - 100(0.02^2 + 0.03^2 + 0.03^2) = 0.78$$

The sensitivity factor, A, is now evaluated as follows.

$$A = t_S \varepsilon Y m_S D F_S = (3000 \text{ s})(0.42)(0.78)(0.98 \text{ g})(0.2667)(1) = 256.9 \text{ g} \cdot \text{s}$$

Next, the MQC can be calculated as shown below.

$$x_Q = \frac{k_Q^2}{2AI_Q}\left(1 + \sqrt{1 + \frac{4I_Q}{k_Q^2}\left(R_B t_S\left(1 + \frac{t_S}{t_B}\right) + 0\right)}\right)$$

$$= \frac{100}{2(256.9\ \text{g}\cdot\text{s})(0.78)}\left(1 + \sqrt{1 + \frac{4(0.78)}{100}\left((0.018\ \text{s}^{-1})(3000\ \text{s})\left(1 + \frac{3000\ \text{s}}{6000\ \text{s}}\right) + 0\right)}\right)$$

$$= 0.718\ \text{Bq/g}$$

Now, as a check, one may use the procedure described in Section 19.5.13 of Chapter 19 to predict the combined standard uncertainty of a measurement made on a hypothetical sample whose analyte concentration is exactly x_Q.

$$N_B = R_B t_B = (0.018\ \text{s}^{-1})(6000\ \text{s}) = 108$$

$$N_S = x_Q A + R_B t_S = (0.718\ \text{Bq/g})(256.9\ \text{g}\cdot\text{s}) + (0.018\ \text{s}^{-1})(3000\ \text{s}) = 238.45$$

$$u_c(X) = \sqrt{\frac{N_S + N_B t_S^2 / t_B^2}{A^2} + x_Q^2\left(\frac{u^2(\varepsilon)}{\varepsilon^2} + \frac{u^2(Y)}{Y^2} + \varphi_{\text{Samp}}^2\right)}$$

$$= \sqrt{\frac{238.45 + (108)(3000\ \text{s})^2 / (6000\ \text{s})^2}{(256.9\ \text{g}\cdot\text{s})^2} + (0.718\ \text{Bq/g})^2\left(0.02^2 + 0.03^2 + 0.03^2\right)}$$

$$= 0.0718\ \text{Bq/g}$$

So, the combined standard uncertainty is predicted to be 0.0718 Bq/g, or 10 % of the true value, as expected.

20.5 References

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ATTACHMENT 20A
Low-Background Detection Issues

20A.1 Overview

This attachment describes methods for determining critical values and minimum detectable concentrations (MDCs) when the standard deviation of the blank signal is not known precisely, which occurs for example when the blank is measured by low-background Poisson counting or when the standard deviation is estimated from a small number of replicate measurements. The methods described below are applicable more generally, even when the background is high or the number of degrees of freedom is large, but in these situations the simpler methods described previously should be adequate.

20A.2 Calculation of the Critical Value

The critical value of the net signal S_C was defined earlier by the relation

$$\Pr[\hat{S} > S_C \mid X = 0] = \alpha \tag{20.33}$$

When the signal assumes only discrete values (e.g., numbers of counts), there may be no value S_C that satisfies Equation 20.33 exactly. The critical value in this case is defined as the smallest value S_C such that $\Pr[\hat{S} > S_C \mid X = 0] \leq \alpha$.

20A.2.1 Normally Distributed Signals

If the distribution of the net signal $\hat{S}$ under H_0 is approximately normal with a well-known standard deviation, σ_0, the critical value of $\hat{S}$ is

$$S_C = z_{1-\alpha}\sigma_0 \tag{20.34}$$

where $z_{1-\alpha}$ denotes the $(1 - \alpha)$-quantile of the standard normal distribution. Typically the standard deviation σ_0 is not well-known and must therefore be replaced by an estimate, $\hat{\sigma}_0$. If $\hat{\sigma}_0$ is determined by a statistical evaluation with v degrees of freedom, the multiplier $z_{1-\alpha}$ should be replaced by $t_{1-\alpha}(v)$, the $(1 - \alpha)$-quantile of the t-distribution with v degrees of freedom (cf. *Type A* evaluation of standard uncertainty in Section 19.4.2.1 of Chapter 19). Thus,

$$S_C = t_{1-\alpha}(v) \times \hat{\sigma}_0 \tag{20.35}$$

Table G.2 in Appendix G lists values of $t_{1-\alpha}(v)$. In general, $t_{1-\alpha}(v)$ is greater than $z_{1-\alpha}$, but the two values are approximately equal if v is large.

When $\hat{B}$ is estimated by the average of n replicate blank measurements (assuming no interferences), the standard deviation $\hat{\sigma}_0$ of the net signal $\hat{S}$ under the null hypothesis may be estimated from the experimental standard deviation of the measured blank values, s_B. Specifically,

$$\hat{\sigma_0} = s_B\sqrt{1 + \frac{1}{n}} \tag{20.36}$$

The number of degrees of freedom, v, in this case equals $n - 1$; so, the critical value of $\hat{S}$ is

$$S_C = t_{1-\alpha}(n-1) \times s_B\sqrt{1 + \frac{1}{n}} \tag{20.37}$$

EXAMPLE 20.9

Problem: Suppose seven replicate blank measurements are made, producing the following results (total counts).

58 43 64 53 47 66 60

Assume the blank distribution is approximately normal and calculate the critical value of the net count (gross sample count minus average blank count) using a 5 % significance level.

Solution: First, calculate the mean blank count, $\overline{B}$.

$$\overline{B} = \frac{1}{n}\sum_{i=1}^{n} B_i = \frac{391}{7} = 55.857$$

Calculate the standard deviation of the blank counts, s_B.

$$s_B = \sqrt{\frac{1}{n-1}\sum_{i=1}^{n}(B_i - \overline{B})^2} = \sqrt{\frac{442.857}{7-1}} = 8.5912$$

Find the 0.95-quantile of the t-distribution with $7 - 1 = 6$ degrees of freedom in Appendix G.

$$t_{1-\alpha}(n-1) = t_{0.95}(6) = 1.943$$

Calculate the critical net count using Equation 20.37.

$$S_C = t_{1-\alpha}(n-1) \times s_B\sqrt{1 + \frac{1}{n}} = 1.943 \times 8.5912\sqrt{1 + \frac{1}{7}} = 17.85$$

Thus, the net count must exceed 17.85 to be considered detected.

Note that if $z_{1-\alpha}$ were used instead of $t_{1-\alpha}(n-1)$ in the equation, the critical value would be underestimated as

$$S_C = z_{1-\alpha} \times s_B \sqrt{1 + \frac{1}{n}} = 1.645 \times 8.5912 \sqrt{1 + \frac{1}{7}} = 15.11 \qquad \text{(incorrect)}$$

20A.2.2 Poisson Counting

It is assumed here, as in Section 20.4, that the instrument is a radiation counter and the instrument signal is the gross count. Therefore,

$$\hat{Y} = N_S \qquad \hat{B} = \left(\frac{N_B}{t_B} + \hat{R}_I \right) t_S \tag{20.38}$$

and the net instrument signal is the net count, which is given by

$$\hat{S} = N_S - \left(\frac{N_B}{t_B} + \hat{R}_I \right) t_S \tag{20.39}$$

where

N_S is the gross count (source count);
N_B is the blank count;
$\hat{R}_I$ is the estimated count rate due to interferences;
t_S is the count time for the test source; and
t_B is the count time for the blank.

If t_B is much greater than t_S, generally at least 10 times greater, the blank count rate, R_B, can be considered to be "well-known," because it contributes little variance to the net signal, $\hat{S}$. The value of R_B may be estimated from a single measurement of long duration or from an average of several measurements of shorter duration. Whenever R_B is well-known, if there are no interferences, then according to the Poisson model, the critical gross count, y_C, equals the smallest nonnegative integer n such that

$$e^{-R_B t_S} \sum_{k=0}^{n} \frac{(R_B t_S)^k}{k!} \geq 1 - \alpha \tag{20.40}$$

Then S_C, the critical net count, equals $y_C - R_B t_S$. Table 20.1 shows critical gross counts for $\alpha = 0.05$ for small values of $R_B t_S$ (adapted from NRC, 1984).[7] To use the table, one calculates the

[7] The breaks in the table occur at $R_B t_S = 0.5 \times \chi^2_{0.05}(2y_C)$ and $0.5 \times \chi^2_{0.05}(2y_C + 2)$.

value of $R_B t_S$, finds the appropriate line in the table, and compares the observed gross count N_S to the value of y_C read from the table. The analyte is considered detected if and only if $N_S > y_C$. When $R_B t_S$ is greater than about 20, y_C may be approximated by

$$y_C = \lfloor 0.5 + R_B t_S + z_{1-\alpha}\sqrt{R_B t_S} \rfloor \tag{20.41}$$

where $z_{1-\alpha}$ denotes the $(1 - \alpha)$-quantile of the standard normal distribution, and for any number x, the expression $\lfloor x \rfloor$ denotes the largest integer not greater than x.

Note that these critical values are appropriate only under the assumption of Poisson counting statistics with no interferences.

TABLE 20.1 — Critical gross count (well-known blank)

$R_B t_S$	y_C	$R_B t_S$	y_C	$R_B t_S$	y_C
0.000–0.051	0	5.425–6.169	10	13.255–14.072	20
0.051–0.355	1	6.169–6.924	11	14.072–14.894	21
0.355–0.818	2	6.924–7.690	12	14.894–15.719	22
0.818–1.366	3	7.690–8.464	13	15.719–16.549	23
1.366–1.970	4	8.464–9.246	14	16.549–17.382	24
1.970–2.613	5	9.246–10.036	15	17.382–18.219	25
2.613–3.285	6	10.036–10.832	16	18.219–19.058	26
3.285–3.981	7	10.832–11.634	17	19.058–19.901	27
3.981–4.695	8	11.634–12.442	18	19.901–20.746	28
4.695–5.425	9	12.442–13.255	19	20.746–21.594	29

Figure 20.2 shows the Type I error rates produced by Table 20.1 for $\alpha = 0.05$ and three different count-time ratios, t_B / t_S. The error rates are much greater than 0.05 when the blank count time equals the sample count time, but they fall as the blank count time increases (and the blank count rate becomes better known). If the blank count rate were known perfectly, the Type I error rate would remain at or below 0.05 everywhere.[8]

[8] Probabilities on the curves are calculated using the equation

$$P(\mu) = 1 - e^{-\mu(1+t_B/t_S)} \sum_{n=0}^{\infty} \frac{(\mu t_B/t_S)^n}{n!} \sum_{k=0}^{y_C(n)} \frac{\mu^k}{k!}$$

where $\mu = R_B t_S$ (the true mean gross count when the sample contains no analyte) and $y_C(n)$ denotes the critical gross count obtained from Table 20.1 when $R_B t_S$ is approximated by $n(t_S / t_B)$.

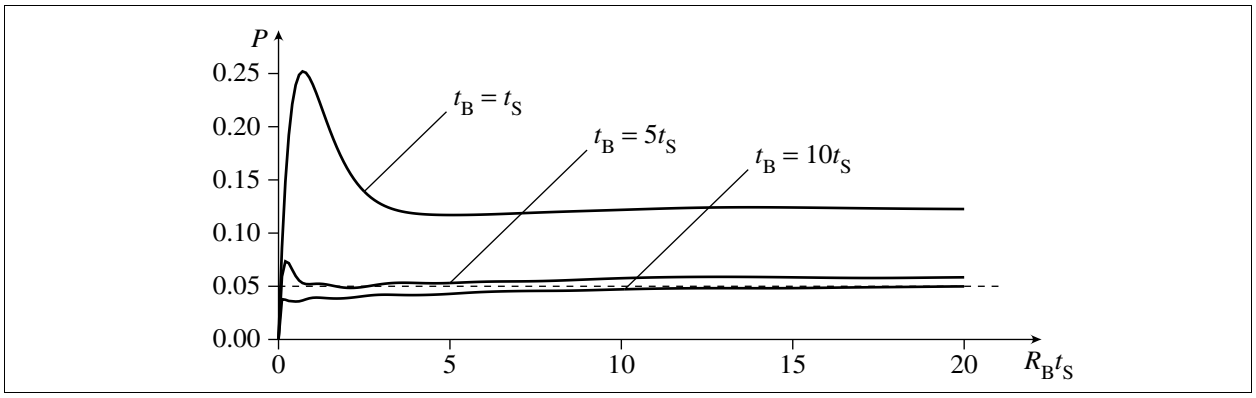

FIGURE 20.2 — Type I error rates for Table 20.1

Other commonly used methods for calculating the critical value when the blank count rate is not well-known are described below.

THE POISSON-NORMAL APPROXIMATION

As stated in Section 20.4.1.2, when Poisson counting statistics are assumed (possibly with additional variance components) and the instrument background remains stable between measurements at a level where the Poisson distribution is approximately normal, the critical net count is given approximately by the equation

$$S_C = z_{1-\alpha} t_S \sqrt{\frac{R_B + R_I}{t_S} + \frac{R_B}{t_B} + \xi_B^2 + \sigma^2(\hat{R}_I)} \tag{20.42}$$

where R_B denotes the (true) mean count rate of the blank, R_I denotes the mean interference count rate, ξ_B^2 denotes non-Poisson variance in the blank (count rate) correction, and $\sigma^2(\hat{R}_I)$ denotes the variance of the estimator for R_I. When there are no interferences and no non-Poisson blank variance, this equation becomes

$$S_C = z_{1-\alpha} \sqrt{R_B t_S \left(1 + \frac{t_S}{t_B}\right)} \tag{20.43}$$

Low mean blank levels cause the Poisson distribution to deviate from the normal model. Figure 20.3 shows the effects of these deviations on the Type I error rates for the Poisson-normal approximation when $t_B = t_S$ and $\alpha = 0.05$. The graph has discontinuities because of the discrete

nature of the Poisson distribution, but the Type I error rate is approximately correct (equal to 0.05) when the mean blank count is 10 or more.[9]

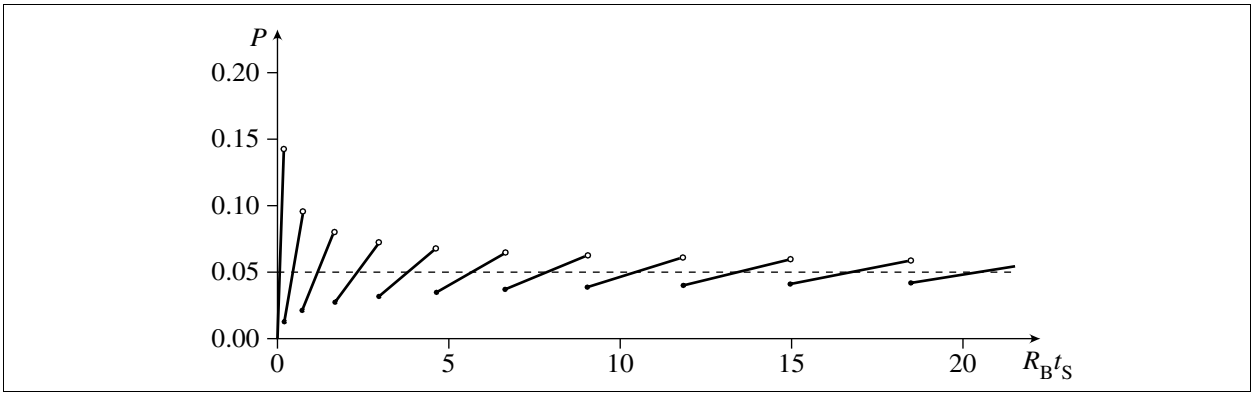

FIGURE 20.3 — Type I error rate for the Poisson-normal approximation ($t_B = t_S$)

In Equation 20.43, R_B denotes the *true* mean blank count rate. In practice, R_B is usually not well-known; so, one must substitute an estimated value, $\hat{R}_B$, as shown in the following equation.

$$S_C = z_{1-\alpha}\sqrt{\hat{R}_B t_S\left(1 + \frac{t_S}{t_B}\right)} \tag{20.44}$$

The most frequently used expressions for S_C may be derived from Equation 20.44 using an estimator $\hat{R}_B$ that equals a weighted average of the measured blank count rate N_B / t_B and the measured source count rate N_S / t_S. A weighted average of both measured rates may be used here to estimate the true blank level for the purpose of the hypothesis test, because, under the null hypothesis of zero net source activity, both measured rates are unbiased estimates of the true blank count rate. Given nonnegative weights w_S and w_B such that $w_S + w_B = 1$, the mean blank count rate is estimated by

$$\hat{R}_B = w_S \frac{N_S}{t_S} + w_B \frac{N_B}{t_B} \tag{20.45}$$

---

[9] Probabilities on the curve are calculated using the equation

$$P(\mu) = 1 - e^{-2\mu}\sum_{n=0}^{\infty}\frac{\mu^n}{n!}\sum_{k=0}^{\lfloor n+2.33\sqrt{\mu}\rfloor}\frac{\mu^k}{k!}$$

where μ denotes the (true) mean blank count. Terms of the infinite sum are accumulated until the cumulative Poisson probability, $e^{-\mu}\sum_{i=0}^{n}\mu^i/i!$, approaches 1. The calculated values agree with those listed in Table 1 of Brodsky (1992). The discontinuities occur at $\mu = k^2 / 2.33^2$ for $k = 1, 2, 3, \ldots$.

This estimator $\hat{R}_B$ is always unbiased under the null hypothesis of zero net activity and no interferences, but the choice of weights affects the variance of the estimator. (When interferences are present, this weighted average is inappropriate.)[10]

This attachment will use the notation $\tilde{S}_C$, which is nonstandard, to denote any version of the critical value that depends on the gross signal N_S (or $\hat{Y}$). Then Equations 20.44 and 20.45 imply the following.

$$\tilde{S}_C = z_{1-\alpha}\sqrt{\left(w_S\frac{N_S}{t_S} + w_B\frac{N_B}{t_B}\right)t_S\left(1 + \frac{t_S}{t_B}\right)} \qquad (20.46)$$

It is often convenient to eliminate N_S from the expression for $\tilde{S}_C$ (e.g., when calculating the MDC). When the same measured value of N_B is used to calculate both the critical value $\tilde{S}_C$ and the net signal $\hat{S}$, elimination of N_S from Equation 20.46 produces the following formula for an alternative critical value S_C.[11]

$$S_C = \frac{z_{1-\alpha}^2 w_S}{2}\left(1 + \frac{t_S}{t_B}\right) + z_{1-\alpha}\sqrt{\frac{z_{1-\alpha}^2 w_S^2}{4}\left(1 + \frac{t_S}{t_B}\right)^2 + N_B\frac{t_S}{t_B}\left(1 + \frac{t_S}{t_B}\right)} \qquad (20.47)$$

It is not generally true that $S_C = \tilde{S}_C$ unless $w_S = 0$, but either critical value may be used to implement the same test for analyte detection, because $\hat{S} > S_C$ if and only if $\hat{S} > \tilde{S}_C$.

If there is additional non-Poisson variance associated with the blank correction, an extra term may be included under the radical (e.g., $\xi_B^2 t_S^2$, where ξ_B^2 is as in Equation 20.42), although at very low blank levels the Poisson variance tends to dominate this excess component.

FORMULA A

The most commonly used approach for calculating S_C is given by Formula A (shown below).

[10] The common practice of using the same Poisson measurement data to calculate both the net signal $\hat{S}$ and its critical value tends to produce a correlation between the two variables. This correlation does not exist when the critical value is determined by a statistical evaluation of normally distributed data as described earlier in the attachment.

[11] The critical value $\tilde{S}_C$ may be written as a function $f(\hat{S})$ of the observed net signal $\hat{S}$ and the blank count N_B. Then $\hat{S}$ exceeds $\tilde{S}_C$ if and only if it exceeds the fixed point of f, which is the value S_C where $f(S_C) = S_C$. The fixed point is a function of N_B but not of N_S.

$$S_C = z_{1-\alpha}\sqrt{N_B \frac{t_S}{t_B}\left(1 + \frac{t_S}{t_B}\right)} \tag{20.48}$$

Formula A

If $\alpha = 0.05$ and $t_B = t_S$, Formula A leads to the well-known expression $2.33\sqrt{N_B}$ for the critical net count (e.g., see Currie, 1968).

Formula A may be derived from Equation 20.44 by using the blank measurement alone to estimate the true blank count rate — i.e., by using the weights $w_S = 0$ and $w_B = 1$.

As noted in Section 20.4.1.2, when the blank count is high (e.g., 100 or more), Formula A works well, but at lower blank levels, it can produce a high rate of Type I errors. Figure 20.4 shows Type I error rates for Formula A as a function of the mean blank count for count time ratios $t_B / t_S = 1$ and 5 when $\alpha = 0.05$.[12]

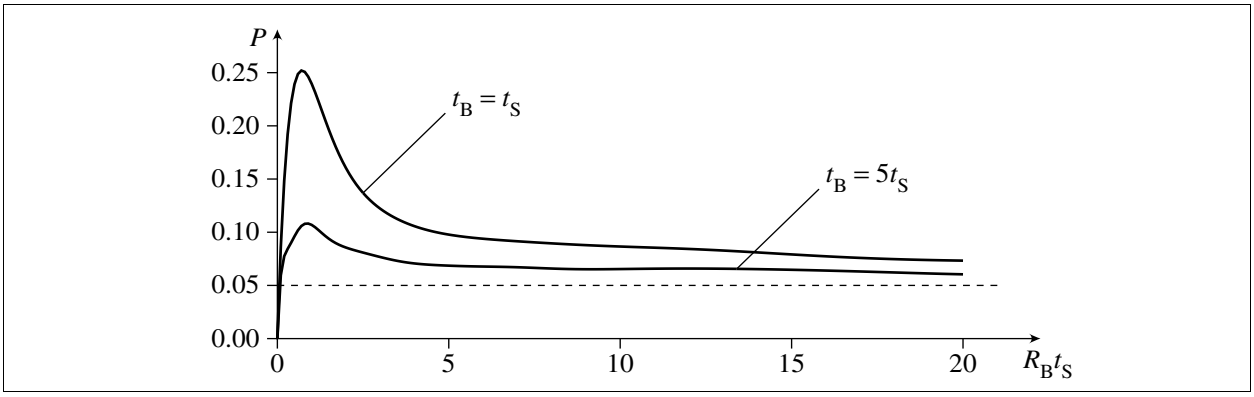

FIGURE 20.4 — Type I error rates for Formula A

[12] Probabilities on the two curves are calculated using the equation

$$P(\mu) = 1 - e^{-\mu(1+t_B/t_S)} \sum_{n=0}^{\infty} \frac{(\mu t_B / t_S)^n}{n!} \sum_{k=0}^{\lfloor y_C(n) \rfloor} \frac{\mu^k}{k!}$$

where $y_C(n) = S_C(n) + n(t_S / t_B)$ and $\mu = R_B t_S$ (the mean gross count when the sample contains no analyte). The same equation with different expressions for $S_C(n)$ is used to calculate the Type I error rates shown in Figures 20.5–8.

FORMULA B

Another published formula for the critical value is (equivalent to) the following (Nicholson, 1966).

$$\tilde{S}_C = z_{1-\alpha}\sqrt{N_S + N_B\frac{t_S^2}{t_B^2}} \tag{20.49}$$

The critical value calculated by Equation 20.49 equals $z_{1-\alpha}$ times the combined standard uncertainty of the net count. This fact is the basis for the original derivation of the formula, but the formula may also be derived from Equation 20.46 using the weights $w_S = t_B / (t_S + t_B)$ and $w_B = t_S / (t_S + t_B)$ to estimate $\hat{R}_B$. When N_S is eliminated from Equation 20.49, one obtains Formula B (below), which is equivalent to the equation for the critical value given in *Atoms, Radiation, and Radiation Protection* (Turner, 1995).

$$S_C = \frac{z_{1-\alpha}^2}{2} + z_{1-\alpha}\sqrt{\frac{z_{1-\alpha}^2}{4} + N_B\frac{t_S}{t_B}\left(1 + \frac{t_S}{t_B}\right)} \tag{20.50}$$

Formula B

Type I error rates for Formula B are shown in Figure 20.5.

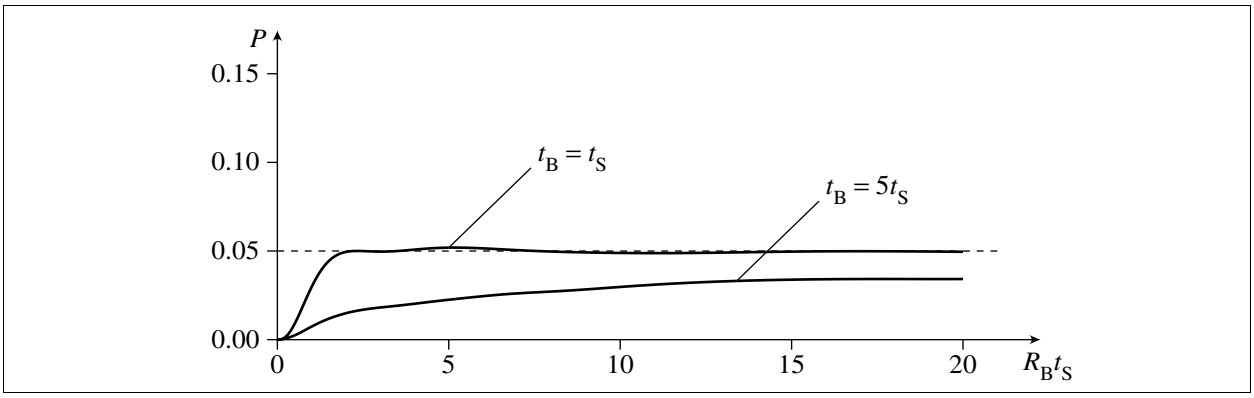

FIGURE 20.5 — Type I error rates for Formula B

Formula B appears natural and intuitive when it is derived in terms of the combined standard uncertainty of the net count, and it gives excellent results when $t_B = t_S$ and the pure Poisson model is valid. However, when the formula is derived using the weights w_S and w_B, as described

above, the expression seems much less natural, because the weights clearly are not optimal when $t_B \neq t_S$. Notice that when $t_B > t_S$, the Type I error rate tends to be less than α.

FORMULA C

If the pure Poisson model is valid, then under the null hypothesis, the weights $w_S = t_S / (t_S + t_B)$ and $w_B = t_B / (t_S + t_B)$ provide the minimum-variance unbiased estimator $\hat{R}_B$ for the mean blank count rate and lead to the following formula for the critical net count (Nicholson, 1963; 1966).[13]

$$\tilde{S}_C = z_{1-\alpha}\sqrt{(N_S + N_B)\frac{t_S}{t_B}} \tag{20.51}$$

Elimination of N_S from Equation 20.51 produces Formula C, shown below.

$$S_C = \frac{z_{1-\alpha}^2 t_S}{2t_B} + z_{1-\alpha}\sqrt{\frac{z_{1-\alpha}^2 t_S^2}{4t_B^2} + N_B\frac{t_S}{t_B}\left(1 + \frac{t_S}{t_B}\right)} \tag{20.52}$$

Formula C

Formula C is equivalent to the equation for the "decision threshold" given in Table 1 of ISO 11929-1 for the case of fixed-time counting. Figure 20.6 shows Type I error rates for Formula C.

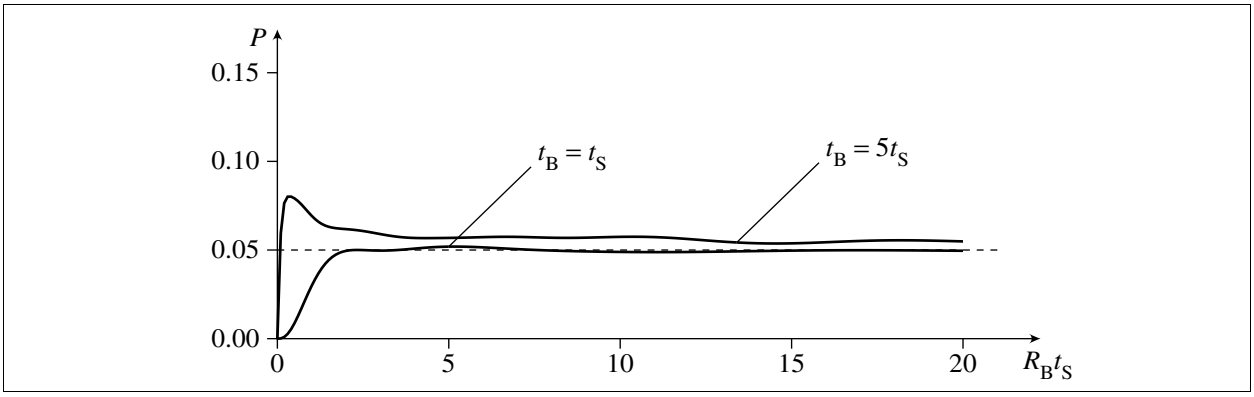

FIGURE 20.6 — Type I error rates for Formula C

[13] The approach here is conceptually similar to that of a two-sample *t*-test, which employs a pooled estimate of variance in the comparison of two normal populations.

If the blank correction involves additional non-Poisson variance, an extra term may be included under the radical in Formula C; however, the weights w_S and w_B used to derive the formula are not necessarily optimal in this case. (See ISO 11929-2 for another approach.)

Note that Formulas B and C are equivalent when $t_B = t_S$, because both assign equal weights to the blank measurement and the source measurement. In this case, both formulas are also equivalent to the formula given by Altshuler and Pasternack (1963).

THE STAPLETON APPROXIMATION

When the mean counts are low and $t_B \neq t_S$, another approximation formula for S_C appears to outperform all of the approximations described above. For small values of the constant d, the statistic

$$Z = 2\left(\sqrt{\frac{N_S + d}{t_S}} - \sqrt{\frac{N_B + d}{t_B}}\right) \Big/ \sqrt{\frac{1}{t_S} + \frac{1}{t_B}} \tag{20.53}$$

which involves variance-stabilizing transformations of the Poisson counts N_S and N_B, has a distribution that is approximately standard normal under the null hypothesis (Stapleton, 1999; Strom and MacLellan, 2001). So, the critical value of Z is $z_{1-\alpha}$, the $(1 - \alpha)$-quantile of the standard normal distribution. From these facts one may derive the following expression for the critical net count as a function of N_B.

$$S_C = d\left(\frac{t_S}{t_B} - 1\right) + \frac{z_{1-\alpha}^2}{4}\left(1 + \frac{t_S}{t_B}\right) + z_{1-\alpha}\sqrt{(N_B + d)\frac{t_S}{t_B}\left(1 + \frac{t_S}{t_B}\right)} \tag{20.54}$$

The Stapleton Approximation

When $\alpha = 0.05$, the value $d = 0.4$ appears to be a near-optimal choice. Then for $t_B = t_S$, the Stapleton approximation gives the equation

$$S_C = 1.35 + 2.33\sqrt{N_B + 0.4} \tag{20.55}$$

Figure 20.7 shows the Type I error rates for the Stapleton approximation when $\alpha = 0.05$ and $d = 0.4$. This approximation gives Type I error rates almost identical to those of Formulas B and C when $t_B = t_S$, but it has an advantage when $t_B \neq t_S$.

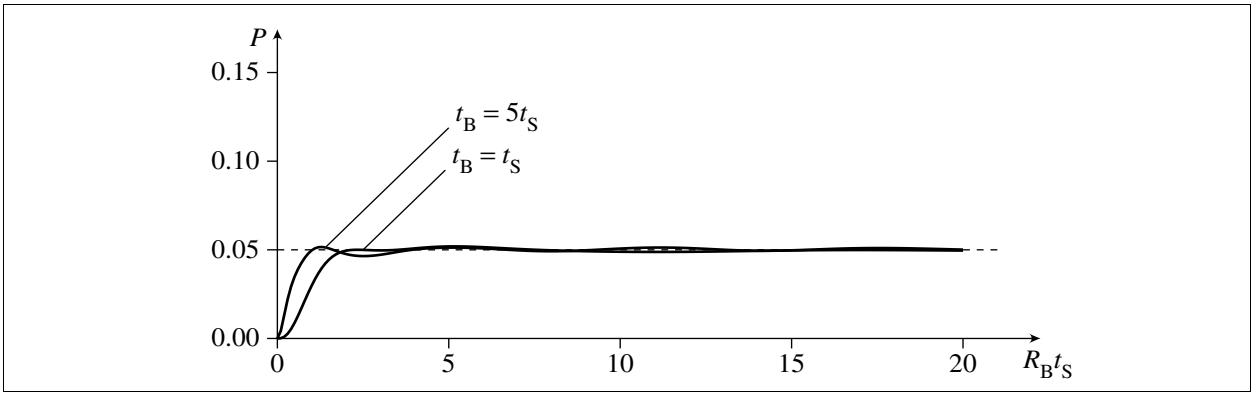

FIGURE 20.7 — Type I error rates for the Stapleton approximation

When $\alpha \neq 0.05$, the value $d = z_{1-\alpha} / 4.112$ appears to give good results ($4.112 = z_{0.95} / 0.4$).

When the blank correction involves a small non-Poisson variance component, a term ($\xi_B^2 t_S^2$) may be included under the radical in Equation 20.54 to account for it.

THE EXACT TEST

Poisson counting statistics also permit an "exact" test for analyte detection, whose Type I error rate is guaranteed to be *no greater than* the chosen value of α, although it may be less. A randomized version of the test can provide a Type I error rate *exactly equal to* α (Nicholson, 1963), but only the nonrandomized version will be considered here, since its outcome is always based solely on the data and not on a random number generator. The test is implemented by rejecting H_0 if and only if the following inequality is true.[14]

$$\sum_{k=N_S}^{N_S+N_B} \binom{N_S + N_B}{k} \left(\frac{t_S}{t_S + t_B}\right)^k \left(\frac{t_B}{t_S + t_B}\right)^{N_S+N_B-k} \leq \alpha \qquad (20.56)$$

NOTE: For any nonnegative integers n and k, the notation $\binom{n}{k}$ denotes a *binomial coefficient*, usually read "n choose k," which is the number of possible combinations of n objects chosen k at a time. For $0 \leq k \leq n$,

[14] The left-hand side of the inequality is a cumulative binomial probability (see Attachment 19A of Chapter 19). It also equals

$$I_{\frac{t_S}{t_S+t_B}}(N_S, N_B + 1)$$

where $I_x(a,b)$ denotes the incomplete beta function (NBS, 1964; Press et al., 1992).

the value of $\binom{n}{k}$ equals $\frac{n!}{k!(n-k)!}$, where the symbol ! denotes the factorial operator. The number of combinations of n objects chosen k at a time is also denoted sometimes by ${}_nC_k$.

Nicholson presents the test as a comparison of the gross count N_S to a critical value. The critical value $\tilde{y}_C$ is the smallest nonnegative integer n such that[15]

$$\sum_{k=0}^{n} \binom{N_S + N_B}{k} \left(\frac{t_S}{t_S + t_B}\right)^k \left(\frac{t_B}{t_S + t_B}\right)^{N_S + N_B - k} \geq 1 - \alpha \qquad (20.57)$$

The same (nonrandomized) test is implemented by calculating a critical gross count, y_C, equal to the smallest nonnegative integer, n, such that

$$\sum_{k=0}^{n} \binom{N_B + k}{N_B} \left(\frac{t_S}{t_S + t_B}\right)^k \geq (1 - \alpha)\left(\frac{t_S + t_B}{t_B}\right)^{N_B + 1} \qquad (20.58)$$

Then the critical net count, S_C, equals $y_C - N_B(t_S / t_B)$. (Note that Inequality 20.58 is intended for use when N_B is small.) Table G.4 in Appendix G lists critical values y_C for $\alpha = 0.01$ and 0.05 and for integral values of the count time ratio, t_B / t_S, ranging from 1 to 5.

Figure 20.8 shows the Type I error rates for the nonrandomized exact test. (The Type I error rate for the randomized version of the test equals 0.05 everywhere.)

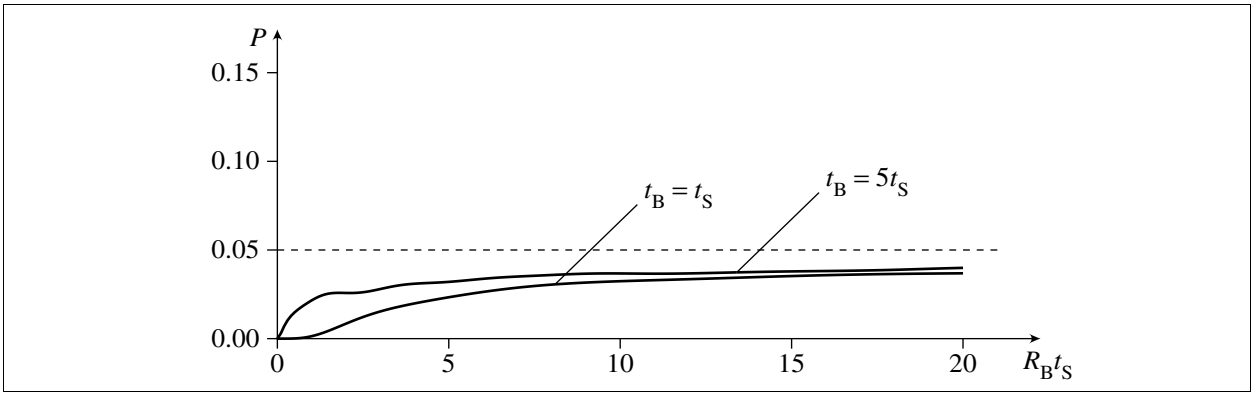

FIGURE 20.8 — Type I error rates for the nonrandomized exact test

[15] To implement the randomized test, calculate the critical value $\tilde{y}_C$, and, if $N_S > \tilde{y}_C$, reject H_0, as in the nonrandomized test. If $N_S = \tilde{y}_C$, calculate a rejection probability P by subtracting $1 - \alpha$ from the sum on the left-hand side of the inequality (with $n = N_S$) and dividing the difference by the summation's last term

$$\binom{N_S + N_B}{N_S} \left(\frac{t_S}{t_S + t_B}\right)^{N_S} \left(\frac{t_B}{t_S + t_B}\right)^{N_B}$$

Then reject H_0 *with probability* P.

EXAMPLE 20.10

Problem: A 60,000-second blank measurement is performed on an alpha-particle spectrometer and 4 counts are observed in a region of interest. A test source is to be counted for 60,000 s. Use the methods described in this attachment to estimate the critical value of the net count when $\alpha = 0.05$.

Solution: Table 20.1 should not be used in this case, because the ratio of count times, t_B / t_S, is too small.

Formula A gives the result

$$S_C = z_{1-\alpha}\sqrt{N_B \frac{t_S}{t_B}\left(1 + \frac{t_S}{t_B}\right)}$$

$$= 1.645\sqrt{4\left(\frac{60{,}000\text{ s}}{60{,}000\text{ s}}\right)\left(1 + \frac{60{,}000\text{ s}}{60{,}000\text{ s}}\right)}$$

$$= 4.65 \text{ net counts.}$$

Formula B gives the result

$$S_C = \frac{z_{1-\alpha}^2}{2} + z_{1-\alpha}\sqrt{\frac{z_{1-\alpha}^2}{4} + N_B \frac{t_S}{t_B}\left(1 + \frac{t_S}{t_B}\right)}$$

$$= \frac{1.645^2}{2} + 1.645\sqrt{\frac{1.645^2}{4} + 4\left(\frac{60{,}000\text{ s}}{60{,}000\text{ s}}\right)\left(1 + \frac{60{,}000\text{ s}}{60{,}000\text{ s}}\right)}$$

$$= 6.20 \text{ net counts.}$$

Formula C gives the result

$$S_C = \frac{z_{1-\alpha}^2 t_S}{2t_B} + z_{1-\alpha}\sqrt{\frac{z_{1-\alpha}^2 t_S^2}{4t_B^2} + N_B \frac{t_S}{t_B}\left(1 + \frac{t_S}{t_B}\right)}$$

$$= \frac{1.645^2(60{,}000\text{ s})}{2(60{,}000\text{ s})} + 1.645\sqrt{\frac{1.645^2(60{,}000\text{ s})^2}{4(60{,}000\text{ s})^2} + 4\left(\frac{60{,}000\text{ s}}{60{,}000\text{ s}}\right)\left(1 + \frac{60{,}000\text{ s}}{60{,}000\text{ s}}\right)}$$

$$= 6.20 \text{ net counts.}$$

Notice that Formula B and Formula C give the same result, because $t_S = t_B$.

The Stapleton approximation (with $d = 0.4$) gives the result

$$S_C = d\left(\frac{t_S}{t_B} - 1\right) + \frac{z_{1-\alpha}^2}{4}\left(1 + \frac{t_S}{t_B}\right) + z_{1-\alpha}\sqrt{(N_B + d)\frac{t_S}{t_B}\left(1 + \frac{t_S}{t_B}\right)}$$

$$= 0.4\left(\frac{60{,}000}{60{,}000} - 1\right) + \frac{1.645^2}{4}\left(1 + \frac{60{,}000}{60{,}000}\right) + 1.645\sqrt{(4 + 0.4)\left(\frac{60{,}000}{60{,}000}\right)\left(1 + \frac{60{,}000}{60{,}000}\right)}$$

$$= 6.23 \text{ net counts.}$$

The exact test gives the result $y_C = 11$ counts (the entry in Table G.4 for $\alpha = 0.05$, $t_B / t_S = 1$, and $N_B = 4$), which implies that

$$S_C = 11 - (4)(60{,}000 / 60{,}000) = 7 \text{ net counts.}$$

EXAMPLE 20.11

Problem: Consider again the problem presented in Example 20.1. A 6000-second blank measurement is performed on a proportional counter and 108 beta counts are observed. A test source is to be counted for 3000 s. Use the methods described in this attachment to estimate the critical value of the net count when $\alpha = 0.05$.

Solution: Again, Table 20.1 should not be used, because the ratio of count times, t_B / t_S, is too small.

Formula A gives the result

$$S_C = z_{1-\alpha}\sqrt{N_B\frac{t_S}{t_B}\left(1 + \frac{t_S}{t_B}\right)}$$

$$= 1.645\sqrt{108\left(\frac{3000}{6000}\right)\left(1 + \frac{3000}{6000}\right)}$$

$$= 14.8 \text{ net counts.}$$

Notice that this is the same result that was obtained in Example 20.1.

Formula B is not recommended. Since $t_B > t_S$ in this case, Formula B produces a Type I error rate that is less than α.

Formula C gives the result

$$S_C = \frac{z_{1-\alpha}^2 t_S}{2t_B} + z_{1-\alpha}\sqrt{\frac{z_{1-\alpha}^2 t_S^2}{4t_B^2} + N_B \frac{t_S}{t_B}\left(1 + \frac{t_S}{t_B}\right)}$$

$$= \frac{(1.645)^2(3000)}{2(6000)} + 1.645\sqrt{\frac{(1.645)^2(3000)^2}{4(6000)^2} + 108\left(\frac{3000}{6000}\right)\left(1 + \frac{3000}{6000}\right)}$$

$$= 15.5 \text{ net counts.}$$

The Stapleton approximation (with $d = 0.4$) gives the result

$$S_C = d\left(\frac{t_S}{t_B} - 1\right) + \frac{z_{1-\alpha}^2}{4}\left(1 + \frac{t_S}{t_B}\right) + z_{1-\alpha}\sqrt{(N_B + d)\frac{t_S}{t_B}\left(1 + \frac{t_S}{t_B}\right)}$$

$$= 0.4\left(\frac{3000}{6000} - 1\right) + \frac{1.645^2}{4}\left(1 + \frac{3000}{6000}\right) + 1.645\sqrt{(108 + 0.4)\left(\frac{3000}{6000}\right)\left(1 + \frac{3000}{6000}\right)}$$

$$= 15.6 \text{ net counts.}$$

The exact test gives the result $y_C = 70$ counts (the entry in Table G.4 for $\alpha = 0.05$, $t_B / t_S = 2$, and $N_B = 108$), which implies that

$$S_C = 70 - (108)(3000 / 6000) = 16 \text{ net counts.}$$

COMPARISONS AND RECOMMENDATIONS

Although Formula A gives the highest Type I error rates of all the formulas described above in the pure Poisson counting scenario, it is the formula that can be adapted most easily for dealing with interferences. It can also be modified to reduce the very high Type I error rates at low blank levels (by adding 1 or 2 to the number of blank counts N_B under the radical). Formula B cannot be recommended. When the pure Poisson model is valid, Formula C gives better results than either A or B, but the Stapleton approximation appears to give the most predictable Type I error rates of all. Nicholson's exact test is the only one of the tests whose Type I error rate is guaranteed not to exceed the chosen significance level, but it is also the most complicated of the tests and requires either software or lookup tables to be practical. Furthermore, the nonrandomized version of the test has relatively low power. Achieving the chosen significance level exactly

appears to require the randomized version of Nicholson's test. Using critical values from Table 20.1 is appropriate when the blank is counted much longer than the sample and the expected count for an analyte-free sample is very low.

MARLAP makes the following recommendations regarding the use of the various equations for the critical value when Poisson statistics are assumed:

- A laboratory should confirm the validity of the Poisson approximation before using Table 20.1, Formula A, Formula C, Stapleton's approximation, Nicholson's exact test, or any other detection criterion that is based on pure Poisson counting statistics. (If the Poisson approximation is invalid, the blank distribution should be determined by repeated measurements.)
- If the blank count time is at least 10 times longer than the sample count time, the critical gross counts in Table 20.1 can be used.
- If the mean blank count is at least 100, Formula A can be used and may be preferred for its relative simplicity.
- Formula B for the critical value should not be used.
- If the ratio of count times, t_B / t_S, is not large, and if the mean blank count is less than 100, either Formula C or Stapleton's approximation should be used. Stapleton's approximation seems to have an advantage over Formula C when $t_S \neq t_B$.
- Nicholson's exact test may be used to compare the means of two Poisson distributions when a high level of statistical rigor is required, but it is more complicated than necessary for routine laboratory analyses and lacks the power of Formula C and Stapleton's approximation.[16]

20A.3 Calculation of the Minimum Detectable Concentration

The minimum detectable concentration, or MDC, was defined earlier as the concentration of analyte, x_D, that must be present in a laboratory sample to give a probability $1 - \beta$ of obtaining a measured response greater than its critical value. Equivalently, the MDC is defined as the analyte concentration x_D that satisfies the relation

$$\Pr[\hat{S} \le S_C \mid X = x_D] = \beta \tag{20.59}$$

where the expression $\Pr[\hat{S} \le S_C \mid X = x_D]$ may be read as "the probability that the net signal $\hat{S}$ does not exceed its critical value S_C when the true concentration X is equal to x_D."

The MDC may be estimated by calculating the minimum detectable value of the net instrument signal, S_D, and converting the result to a concentration. Recall that the minimum detectable value

[16] The reduced power of the exact test at low blank levels is evident from the low Type I error rates shown in Figure 20.8.

of the net instrument signal is defined as the mean value of the net signal that gives a specified probability, $1 - \beta$, of yielding an observed signal greater than its critical value S_C. Thus,

$$\Pr[\hat{S} \le S_C \mid S = S_D] = \beta \tag{20.60}$$

where S denotes the true mean net signal.

20A.3.1 Normally Distributed Signals

If the net signal, $\hat{S}$, is normally distributed and its estimated standard deviation, $\hat{\sigma}_0$, under H_0 is determined from a statistical evaluation with ν degrees of freedom (e.g., $n = \nu + 1$ replicate blank measurements), then the critical value of $\hat{S}$ is

$$S_C = t_{1-\alpha}(\nu) \times \hat{\sigma}_0 \tag{20.61}$$

Then, if the variance of $\hat{S}$ is constant at all concentrations – or at least can be considered constant at sufficiently low concentrations – the minimum detectable value of the signal is given by

$$S_D = \delta_{\alpha,\beta,\nu}\sigma_0 \tag{20.62}$$

where $\delta_{\alpha,\beta,\nu}$ denotes the noncentrality parameter of a noncentral t-distribution with ν degrees of freedom. The parameter $\delta_{\alpha,\beta,\nu}$ is such that

$$t'_{\beta}(\nu, \delta_{\alpha,\beta,\nu}) = t_{1-\alpha}(\nu) \tag{20.63}$$

where $t'_{\beta}(\nu, \delta_{\alpha,\beta,\nu})$ denotes the β-quantile of the noncentral t-distribution. The noncentrality parameter $\delta_{\alpha,\beta,\nu}$ may be approximated by

$$\delta_{\alpha,\beta,\nu} \approx t_{1-\alpha}(\nu) \times \left(1 - \frac{1}{4\nu}\right) + z_{1-\beta}\sqrt{1 + \frac{t_{1-\alpha}(\nu)^2}{2\nu}} \tag{20.64}$$

which is based on an approximation for the noncentral t distribution function (NBS, 1964). When $\alpha = \beta = 0.05$ and $\nu \ge 4$, the noncentrality parameter is also approximated adequately by $t_{0.95}(\nu) \times 8\nu / (4\nu + 1)$ (Currie, 1997).

Conceptually the standard deviation $\hat{\sigma}_0$ used to calculate the critical value, S_C, is only an estimate and therefore can be considered a random variable. If it were the true standard deviation, the correct multiplier used to calculate S_C would be $z_{1-\alpha}$, not $t_{1-\alpha}(\nu)$. However, the standard deviation used to calculate S_D is, conceptually at least, the true standard deviation σ_0, even if its value is not known exactly. The true standard deviation may be estimated by $\hat{\sigma}_0$, but since the estimator $\hat{\sigma}_0$ is

biased, a correction factor should be used for ν less than about 20.[17] An unbiased estimator for σ_0 is $\hat{\sigma}_0 \,/\, c_4$, where

$$c_4 = \frac{\Gamma\left(\frac{\nu+1}{2}\right)}{\Gamma\left(\frac{\nu}{2}\right)}\sqrt{\frac{2}{\nu}} \tag{20.65}$$

and where Γ denotes the *gamma function* (NBS, 1964). The gamma function is easily computed in software (Press et al., 1992), but c_4 is also approximated well by $4\nu / (4\nu + 1)$, and values of c_4 are commonly tabulated in references for statistical quality control (whence the notation c_4 is borrowed). Then S_D is estimated by

$$S_D = \delta_{\alpha,\beta,\nu}\frac{\hat{\sigma}_0}{c_4} \tag{20.66}$$

which is approximately $2\,t_{0.95}(\nu)\hat{\sigma}_0$, or $2\,S_C$, when $\alpha = \beta = 0.05$ and $\nu \geq 4$. Values of c_4 for $\nu = 1$ to 40 are listed in Table 20.2.

TABLE 20.2 — Bias factor for the experimental standard deviation

ν	c_4	ν	c_4	ν	c_4	ν	c_4
1	0.79788	11	0.97756	21	0.98817	31	0.99197
2	0.88623	12	0.97941	22	0.98870	32	0.99222
3	0.92132	13	0.98097	23	0.98919	33	0.99245
4	0.93999	14	0.98232	24	0.98964	34	0.99268
5	0.95153	15	0.98348	25	0.99005	35	0.99288
6	0.95937	16	0.98451	26	0.99043	36	0.99308
7	0.96503	17	0.98541	27	0.99079	37	0.99327
8	0.96931	18	0.98621	28	0.99111	38	0.99344
9	0.97266	19	0.98693	29	0.99142	39	0.99361
10	0.97535	20	0.98758	30	0.99170	40	0.99377

EXAMPLE 20.12

Problem: Use the blank data from Example 20.10 to calculate the minimum detectable net signal, S_D. Assume the variance of the net signal, $\hat{S}$, is approximately constant at low analyte concentrations.

[17] Although $\hat{\sigma}_0^2$ is assumed here to be an unbiased estimator for the variance, its square root, $\hat{\sigma}_0$, is a biased estimator for the standard deviation (see Section 19.4.5.2 in Chapter 19).

Solution: In Example 20.9 the standard deviation of the blank, s_B, based on seven replicate measurements was found to be 8.5912. The estimated standard deviation of the net signal therefore is

$$\hat{\sigma_0} = (8.5912)\sqrt{1 + \frac{1}{7}} = 9.1844$$

The number of degrees of freedom, v, equals $7 - 1 = 6$. So, the value of the noncentrality parameter, $\delta_{\alpha,\beta,v}$, may be approximated as follows.

$$t_{1-\alpha}(v) = t_{0.95}(6) = 1.943$$

$$\begin{aligned}\delta_{\alpha,\beta,v} &= t_{1-\alpha}(v) \times \left(1 - \frac{1}{4v}\right) + z_{1-\alpha}\sqrt{1 + \frac{t_{1-\alpha}(v)^2}{2v}} \\ &= 1.943 \times \left(1 - \frac{1}{(4)(6)}\right) + 1.645\sqrt{1 + \frac{1.943^2}{(2)(6)}} \\ &= 3.748\end{aligned}$$

The value of c_4 for 6 degrees of freedom is 0.95937. So,

$$S_D = \delta_{\alpha,\beta,v}\frac{\hat{\sigma_0}}{c_4} = (3.748)\frac{9.1844}{0.95937} = 35.88.$$

If the variance of $\hat{S}$ is not constant but increases with the mean signal S, the minimum detectable net signal is determined implicitly by the equation

$$t'_{\beta}\left(v, \frac{S_D}{\sigma_D}\right) = t_{1-\alpha}(v) \times \frac{\sigma_0}{\sigma_D} \tag{20.67}$$

where σ_D denotes the standard deviation of $\hat{S}$ when $S = S_D$. An iterative algorithm, such as the one shown below, may be needed to solve the equation for S_D.

1. Set $\sigma_0 = \sqrt{\sigma^2(\hat{S} \mid S = 0)}$
2. Initially calculate $S_D = t_{1-\alpha}(v) \times \sigma_0$
3. **repeat loop (Lines 4–7)**
4. Set $\sigma_D = \sqrt{\sigma^2(\hat{S} \mid S = S_D)}$

5. Find the value of δ such that $t'_{\beta}(\nu, \delta) = t_{1-\alpha}(\nu) \times \sigma_0 / \sigma_D$
6. Set $h = S_D$
7. Recalculate $S_D = \delta \sigma_D$
8. **until** $|S_D - h|$ is sufficiently small
9. **output** the solution S_D

The value of the noncentrality parameter δ in Step 5 may be approximated by

$$\delta \approx \left(t_{1-\alpha}(\nu) \times \frac{\sigma_0}{\sigma_D} \right) \left(1 - \frac{1}{4\nu} \right) + z_{1-\beta} \sqrt{1 + \frac{\left(t_{1-\alpha}(\nu) \times \sigma_0 / \sigma_D \right)^2}{2\nu}} \qquad (20.68)$$

When $\hat{\sigma}_0$ is determined by any means other than a statistical evaluation, S_D must be calculated differently.

EXAMPLE 20.13

Problem: Assume the signal, $\hat{S}$, is the net count for a radioactivity measurement, and its variance is given by an expression of the form

$$aS^2 + bS + c$$

The coefficient b is assumed to be 1, because the term bS represents the Poisson counting variance due to activity in the sample (see Section 20.4.2.2). The term c is estimated by $\hat{\sigma}_0^2$, the variance of the net signal observed when analyte-free samples are analyzed. The coefficient a is estimated to be 0.05^2, and represents a 5 % coefficient of variation, which is observed at high analyte concentrations. Assume $\hat{\sigma}_0$ is evaluated from 7 replicate blank measurements and is found to be 9.1844, as in the preceding example. Use the iterative algorithm described above to approximate the minimum detectable net signal, S_D.

Solution: The first two steps are performed as follows.

$$\sigma_0 = 9.1844$$
$$S_D = 1.943 \times 9.1844 = 17.85$$

Then the first iteration of the loop is performed as follows.

$$\sigma_D = \sqrt{(0.05)^2(17.85)^2 + 17.85 + (9.1844)^2} = 10.149$$

$$t_{1-\alpha}(v) \times \frac{\sigma_0}{\sigma_D} = 1.943 \times \frac{9.1844}{10.149} = 1.7584$$

$$\delta = 1.7584 \times \left(1 - \frac{1}{(4)(6)}\right) + 1.645\sqrt{1 + \frac{1.7584^2}{(2)(6)}} = 3.5298$$

$$S_D = (3.5298)(10.149) = 35.822$$

Subsequent iterations produce the sequence of approximations

37.242 37.354 37.363 37.364 37.364 ...

The sequence converges to 37.364, which is the approximate value of the minimum detectable net signal.

20A.3.2 Poisson Counting

Another equation for S_D, which was described in Section 20.4.2.2, is

$$S_D = S_C + z_{1-\beta}\sqrt{\sigma^2(\hat{S} \mid S = S_D)} \tag{20.69}$$

where $S_C = z_{1-\alpha}\sigma_0$ and $\sigma^2(\hat{S} \mid S = S_D)$ denotes the variance of the measured signal, $\hat{S}$, when the true mean signal, S, equals S_D. This equation is the basis for formulas that are commonly used for S_D when the Poisson-normal approximation is assumed. Regardless of whether the signal follows the pure Poisson model or has non-Poisson variance, the variance of $\hat{S}$ can usually be expressed in the form

$$\sigma^2(\hat{S}) = aS^2 + bS + c \tag{20.70}$$

as in Example 20.13, where S denotes the true mean net signal and the constants a, b, and c do not depend on S. In this case, the minimum detectable net signal is given by

$$S_D = \frac{1}{I_\beta}\left(S_C + \frac{z_{1-\beta}^2 b}{2} + z_{1-\beta}\sqrt{bS_C + \frac{z_{1-\beta}^2 b^2}{4} + aS_C^2 + I_\beta c}\right) \tag{20.71}$$

where $I_\beta = 1 - z_{1-\beta}^2 a$.

Equation 20.69 is often used even when S_C is calculated using one of the formulas presented above for low-background Poisson counting, with $R_B t_B$ substituted for the blank count N_B, but in this case S_D may be underestimated because of the fact that the calculated value of S_C varies from measurement to measurement. One option for obtaining a more conservative estimate of S_D is to substitute a conservative value of S_C, which will be denoted here by $[S_C]$. For Poisson counting, one method of obtaining $[S_C]$ is to use the value of S_C calculated from the largest blank count N_B likely to be observed, given the assumed mean blank count rate R_B (e.g., use Table 20.1 with $R_B t_B$ replacing $R_B t_S$ and N_B replacing y_C in the column headings). To calculate S_D, one may substitute $[S_C]$ for S_C in Equation 20.71.

Note that $[S_C]$ is not used to make detection decisions. It is used only to calculate S_D.

For example, suppose $\alpha = \beta = 0.05$, the assumed mean blank count rate is $R_B = 8 \times 10^{-4}$ s^{-1}, and the blank count time is $t_B = 6000$ s. Then $R_B t_B = 4.8$ counts. Using Table 20.1, one finds 4.8 in the first column between 4.695 and 5.425, and reads the value 9 from the second column. So, 9 is the largest value of N_B likely to be observed when measuring a blank. Now, if Stapleton's approximation is used to calculate S_C when making a detection decision, the value of $[S_C]$ used to calculate S_D is given by the following equation.

$$[S_C] = 0.4\left(\frac{t_S}{t_B} - 1\right) + \frac{1.645^2}{4}\left(1 + \frac{t_S}{t_B}\right) + 1.645\sqrt{(9 + 0.4)\frac{t_S}{t_B}\left(1 + \frac{t_S}{t_B}\right)} \qquad (20.72)$$

So, if $t_S = t_B$, then $[S_C] = 8.49$ counts.

PURE POISSON COUNTING

As previously noted, counting data never follow the Poisson model exactly, but the model can be used to calculate S_D if the variance of the blank signal is approximately Poisson and a conservative value of the sensitivity factor is used to convert S_D to x_D. Equation 20.28, which is repeated below as Equation 20.73, shows how to calculate S_D using the pure Poisson model.

$$S_D = S_C + \frac{z_{1-\beta}^2}{2} + z_{1-\beta}\sqrt{\frac{z_{1-\beta}^2}{4} + S_C + R_B t_S\left(1 + \frac{t_S}{t_B}\right)} \qquad (20.73)$$

When Formula A is used for the critical net count, and $\alpha = \beta$, this expression for S_D simplifies to $z_{1-\beta}^2 + 2S_C$. Example 20.5 in Section 20.4.2.3 illustrates the use of the latter expression.

DETECTION LIMITS FOR THE STAPLETON APPROXIMATION

When the Stapleton approximation is used for S_C, the minimum detectable net count S_D may be calculated using Equation 20.73, but when the pure Poisson model is assumed, a better estimate is given by the formula

$$S_D = \frac{(z_{1-\alpha} + z_{1-\beta})^2}{4}\left(1 + \frac{t_S}{t_B}\right) + (z_{1-\alpha} + z_{1-\beta})\sqrt{R_B t_S\left(1 + \frac{t_S}{t_B}\right)} \tag{20.74}$$

Equation 20.74 also gives a better approximation of S_D even when Formula C is used for the critical value as long as the ratio of count times t_B / t_S is not too far from 1 (see Table 20.3). It is recommended by ISO 11929-1 in a slightly different but equivalent form.

When $\alpha = \beta = 0.05$ and $t_B = t_S$, the preceding equation becomes

$$S_D = 5.41 + 4.65\sqrt{R_B t_S} \tag{20.75}$$

PRECISE CALCULATION OF S_D

When the pure Poisson model is assumed, with no other sources of variance, the mean blank count rate R_B and the analyte detection criteria completely determine S_D. So, in principle, a computer program can be written to calculate S_D precisely. The calculation is most easily described when the critical net count is expressed in terms of N_B but not N_S (e.g., S_C as defined by Formulas A–C, the Stapleton approximation, and the exact test). Then, at any specified value S of the mean net signal, the power of the detection test can be computed using either of the following expressions:

$$\begin{aligned} Power &= 1 - \sum_{n=0}^{\infty} \frac{(R_B t_B)^n e^{-R_B t_B}}{n!} \sum_{k=0}^{\lfloor y_C(n) \rfloor} \frac{(R_B t_S + S)^k e^{-(R_B t_S + S)}}{k!} \\ &= 1 - \exp(-R_B(t_S + t_B) - S) \sum_{n=0}^{\infty} \frac{(R_B t_B)^n}{n!} \sum_{k=0}^{\lfloor y_C(n) \rfloor} \frac{(R_B t_S + S)^k}{k!} \end{aligned} \tag{20.76}$$

where $y_C(n)$ denotes the value of y_C (or $S_C + N_B t_S / t_B$) when $N_B = n$. Terms of the infinite sum must be accumulated only until the cumulative Poisson probability, $e^{-R_B t_B} \sum_{m=0}^{n} (R_B t_B)^m / m!$, approaches 1. Given a software procedure to compute Equation 20.76, the value of S_D may be determined using an iterative algorithm, such as Newton's method or bisection, which calculates

the power at trial values of S until the correct value is found where the power equals $1 - \beta$ (e.g. see Burden and Faires, 1993).

Since no sources of variance except Poisson counting statistics are being considered here, a conservative value of the sensitivity factor should be used when converting S_D to the minimum detectable concentration, x_D.

A procedure of the type described above generated the true values of S_D for Table 20.3, which shows both the estimated and true values of S_D obtained when Formulas A and C and the Stapleton approximation are used for the critical value. The estimated values of S_D in this table are based on values of S_C calculated using the true mean blank count, not the upper bound $[N_B]$. The use of $[N_B]$ would produce larger estimates.

If one can assume that the sensitivity, A, has a particular distribution, such as a rectangular or triangular distribution, then it is still possible to calculate S_D precisely in software, although the mathematics is less straightforward than that needed when only Poisson variance is considered. At any specified value, S, of the mean net signal, the detection power equals

$$Power = 1 - e^{-R_B t_B} \sum_{n=0}^{\infty} \frac{(R_B t_B)^n}{n!} \sum_{k=0}^{\lfloor y_C(n) \rfloor} f(k;S) \qquad (20.77)$$

where $f(k,S)$ is the probability that the gross count will equal k when the mean net signal is S. Given an assumed distribution for A, the value of $f(k,S)$ can be calculated in software. For example, if the sensitivity has a rectangular distribution with mean μ_A and half-width δ, then

$$f(k;S) = \frac{1}{2\delta x}\left(P\left(k+1,\, R_B t_S + S\left(1 + \frac{\delta}{\mu_A}\right)\right) - P\left(k+1,\, R_B t_S + S\left(1 - \frac{\delta}{\mu_A}\right)\right)\right) \qquad (20.78)$$

where $P(\cdot,\cdot)$ denotes the incomplete gamma function. Other combinations of the incomplete gamma function appear when different polygonal distributions are assumed (e.g., triangular).

To the extent that this approach accounts for the variance of the sensitivity, A, it becomes unnecessary to assume a conservative value of A when converting S_D to x_D. Instead, one uses the best available estimates of the actual distribution parameters (e.g., μ_A and δ above).

TABLE 20.3 — Estimated and true values of S_D ($t_B = t_S$)

Mean Blank Count	Formula A		Formula C		Stapleton	
	Estimated by Eq. 20.73	True	Estimated by Eq. 20.73	True	Estimated by Eq. 20.74	True
0	2.706	2.996	7.083	6.296	5.411	6.296
1	7.358	8.351	9.660	10.095	10.063	10.095
2	9.285	10.344	11.355	12.010	11.991	12.010
3	10.764	11.793	12.719	13.551	13.469	13.551
4	12.010	13.021	13.894	14.826	14.716	14.826
5	13.109	14.091	14.942	15.930	15.814	15.930
6	14.101	15.076	15.897	16.902	16.807	16.902
7	15.015	16.028	16.780	17.785	17.720	17.785
8	15.864	16.945	17.605	18.614	18.570	18.614
9	16.663	17.804	18.383	19.406	19.368	19.406
10	17.418	18.595	19.120	20.170	20.123	20.170
11	18.136	19.324	19.823	20.903	20.841	20.903
12	18.822	20.002	20.496	21.602	21.527	21.602
13	19.480	20.642	21.142	22.267	22.185	22.267
14	20.113	21.257	21.764	22.900	22.819	22.900
15	20.724	21.854	22.366	23.506	23.430	23.506
16	21.315	22.438	22.948	24.091	24.020	24.091
17	21.888	23.010	23.513	24.657	24.593	24.657
18	22.444	23.569	24.062	25.206	25.149	25.206
19	22.985	24.116	24.596	25.738	25.690	25.738
20	23.511	24.649	25.116	26.252	26.217	26.252

20A.4 References

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APPENDIX G
STATISTICAL TABLES

Table G.1 — Quantiles of the standard normal distribution

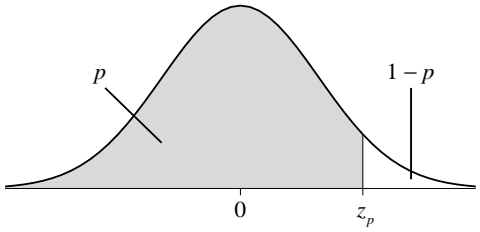
p	$1 - p$	z_p	p	$1 - p$	z_p
0.51	0.49	0.02507	0.76	0.24	0.7063
0.52	0.48	0.05015	0.77	0.23	0.7388
0.53	0.47	0.07527	0.78	0.22	0.7722
0.54	0.46	0.1004	0.79	0.21	0.8064
0.55	0.45	0.1257	0.80	0.20	0.8416
0.56	0.44	0.1510	0.81	0.19	0.8779
0.57	0.43	0.1764	0.82	0.18	0.9154
0.58	0.42	0.2019	0.83	0.17	0.9542
0.59	0.41	0.2275	0.84	0.16	0.9945
0.60	0.40	0.2533	0.85	0.15	1.036
0.61	0.39	0.2793	0.86	0.14	1.080
0.62	0.38	0.3055	0.87	0.13	1.126
0.63	0.37	0.3319	0.88	0.12	1.175
0.64	0.36	0.3585	0.89	0.11	1.227
0.65	0.35	0.3853	0.90	0.10	1.282
0.66	0.34	0.4125	0.91	0.09	1.341
0.67	0.33	0.4399	0.92	0.08	1.405
0.68	0.32	0.4677	0.93	0.07	1.476
0.69	0.31	0.4959	0.94	0.06	1.555
0.70	0.30	0.5244	0.95	0.05	1.645
0.71	0.29	0.5534	0.96	0.04	1.751
0.72	0.28	0.5828	0.97	0.03	1.881
0.73	0.27	0.6128	0.98	0.02	2.054
0.74	0.26	0.6433	0.99	0.01	2.326
0.75	0.25	0.6745	1.00	0.00	∞

Note: $z_{1-p} = -z_p$

(Continued on next page)

Table G.1 (Continued) — Quantiles of the standard normal distribution

p	$1 - p$	z_p
0.90	0.10	1.282
0.95	0.05	1.645
0.975	0.025	1.960
0.99	0.01	2.326
0.995	0.005	2.576
0.9975	0.0025	2.807
0.999	0.001	3.090
0.9995	0.0005	3.291
0.99975	0.00025	3.481
0.9999	0.0001	3.719



$$p = \Phi(z_p) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{z_p} e^{-x^2/2}\,dx = \frac{1}{2} + \frac{e^{-z_p^2/2}}{\sqrt{2\pi}}\left(z_p + \frac{z_p^3}{3} + \frac{z_p^5}{3\cdot 5} + \frac{z_p^7}{3\cdot 5\cdot 7} + \cdots\right)$$

Table G.2 — Quantiles of Student's *t* distribution

Degrees of Freedom	$p = 0.90$ $1 - p = 0.10$	0.95 0.05	0.975 0.025	0.98 0.02	0.99 0.01	0.995 0.005	0.9975 0.0025
1	$t_p =$ 3.078	6.314	12.706	15.895	31.821	63.657	127.321
2	1.886	2.920	4.303	4.849	6.965	9.925	14.089
3	1.638	2.353	3.182	3.482	4.541	5.841	7.453
4	1.533	2.132	2.776	2.999	3.747	4.604	5.598
5	1.476	2.015	2.571	2.757	3.365	4.032	4.773
6	1.440	1.943	2.447	2.612	3.143	3.707	4.317
7	1.415	1.895	2.365	2.517	2.998	3.499	4.029
8	1.397	1.860	2.306	2.449	2.896	3.355	3.833
9	1.383	1.833	2.262	2.398	2.821	3.250	3.690
10	1.372	1.812	2.228	2.359	2.764	3.169	3.581
11	1.363	1.796	2.201	2.328	2.718	3.106	3.497
12	1.356	1.782	2.179	2.303	2.681	3.055	3.428
13	1.350	1.771	2.160	2.282	2.650	3.012	3.372
14	1.345	1.761	2.145	2.264	2.624	2.977	3.326
15	1.341	1.753	2.131	2.249	2.602	2.947	3.286
16	1.337	1.746	2.120	2.235	2.583	2.921	3.252
17	1.333	1.740	2.110	2.224	2.567	2.898	3.222
18	1.330	1.734	2.101	2.214	2.552	2.878	3.197
19	1.328	1.729	2.093	2.205	2.539	2.861	3.174
20	1.325	1.725	2.086	2.197	2.528	2.845	3.153
21	1.323	1.721	2.080	2.189	2.518	2.831	3.135
22	1.321	1.717	2.074	2.183	2.508	2.819	3.119
23	1.319	1.714	2.069	2.177	2.500	2.807	3.104
24	1.318	1.711	2.064	2.172	2.492	2.797	3.091
25	1.316	1.708	2.060	2.167	2.485	2.787	3.078
26	1.315	1.706	2.056	2.162	2.479	2.779	3.067
27	1.314	1.703	2.052	2.158	2.473	2.771	3.057
28	1.313	1.701	2.048	2.154	2.467	2.763	3.047
29	1.311	1.699	2.045	2.150	2.462	2.756	3.038
30	1.310	1.697	2.042	2.147	2.457	2.750	3.030

Table G.2 (Continued) — Quantiles of Student's *t* distribution

Degrees of Freedom	$p = 0.90$ $1 - p = 0.10$	0.95 0.05	0.975 0.025	0.98 0.02	0.99 0.01	0.995 0.005	0.9975 0.0025
31	1.309	1.696	2.040	2.144	2.453	2.744	3.022
32	1.309	1.694	2.037	2.141	2.449	2.738	3.015
33	1.308	1.692	2.035	2.138	2.445	2.733	3.008
34	1.307	1.691	2.032	2.136	2.441	2.728	3.002
35	1.306	1.690	2.030	2.133	2.438	2.724	2.996
36	1.306	1.688	2.028	2.131	2.434	2.719	2.990
37	1.305	1.687	2.026	2.129	2.431	2.715	2.985
38	1.304	1.686	2.024	2.127	2.429	2.712	2.980
39	1.304	1.685	2.023	2.125	2.426	2.708	2.976
40	1.303	1.684	2.021	2.123	2.423	2.704	2.971
41	1.303	1.683	2.020	2.121	2.421	2.701	2.967
42	1.302	1.682	2.018	2.120	2.418	2.698	2.963
43	1.302	1.681	2.017	2.118	2.416	2.695	2.959
44	1.301	1.680	2.015	2.116	2.414	2.692	2.956
45	1.301	1.679	2.014	2.115	2.412	2.690	2.952
46	1.300	1.679	2.013	2.114	2.410	2.687	2.949
47	1.300	1.678	2.012	2.112	2.408	2.685	2.946
48	1.299	1.677	2.011	2.111	2.407	2.682	2.943
49	1.299	1.677	2.010	2.110	2.405	2.680	2.940
50	1.299	1.676	2.009	2.109	2.403	2.678	2.937
60	1.296	1.671	2.000	2.099	2.390	2.660	2.915
70	1.294	1.667	1.994	2.093	2.381	2.648	2.899
80	1.292	1.664	1.990	2.088	2.374	2.639	2.887
90	1.291	1.662	1.987	2.084	2.368	2.632	2.878
100	1.290	1.660	1.984	2.081	2.364	2.626	2.871
200	1.286	1.653	1.972	2.067	2.345	2.601	2.839
300	1.284	1.650	1.968	2.063	2.339	2.592	2.828
400	1.284	1.649	1.966	2.060	2.336	2.588	2.823
500	1.283	1.648	1.965	2.059	2.334	2.586	2.820
∞	1.282	1.645	1.960	2.054	2.326	2.576	2.807

Table G.3 — Quantiles of chi-square

Degrees of Freedom	Lower Tail Probability											
	0.0025	**0.0050**	**0.0100**	**0.0250**	**0.0500**	**0.1000**	**0.9000**	**0.9500**	**0.9750**	**0.9900**	**0.9950**	**0.9975**
1	9.82e−6	3.93e−5	1.57e−4	9.82e−4	3.93e−3	0.0158	2.71	3.84	5.02	6.63	7.88	9.14
2	5.01e−3	0.0100	0.0201	0.0506	0.103	0.211	4.61	5.99	7.38	9.21	10.60	11.98
3	0.0449	0.0717	0.115	0.216	0.352	0.584	6.25	7.81	9.35	11.34	12.84	14.32
4	0.145	0.207	0.297	0.484	0.711	1.06	7.78	9.49	11.14	13.28	14.86	16.42
5	0.307	0.412	0.554	0.831	1.15	1.61	9.24	11.07	12.83	15.09	16.75	18.39
6	0.527	0.676	0.872	1.24	1.64	2.20	10.64	12.59	14.45	16.81	18.55	20.25
7	0.794	0.989	1.24	1.69	2.17	2.83	12.02	14.07	16.01	18.48	20.28	22.04
8	1.10	1.34	1.65	2.18	2.73	3.49	13.36	15.51	17.53	20.09	21.95	23.77
9	1.45	1.73	2.09	2.70	3.33	4.17	14.68	16.92	19.02	21.67	23.59	25.46
10	1.83	2.16	2.56	3.25	3.94	4.87	15.99	18.31	20.48	23.21	25.19	27.11
11	2.23	2.60	3.05	3.82	4.57	5.58	17.28	19.68	21.92	24.72	26.76	28.73
12	2.66	3.07	3.57	4.40	5.23	6.30	18.55	21.03	23.34	26.22	28.30	30.32
13	3.11	3.57	4.11	5.01	5.89	7.04	19.81	22.36	24.74	27.69	29.82	31.88
14	3.58	4.07	4.66	5.63	6.57	7.79	21.06	23.68	26.12	29.14	31.32	33.43
15	4.07	4.60	5.23	6.26	7.26	8.55	22.31	25.00	27.49	30.58	32.80	34.95
16	4.57	5.14	5.81	6.91	7.96	9.31	23.54	26.30	28.85	32.00	34.27	36.46
17	5.09	5.70	6.41	7.56	8.67	10.09	24.77	27.59	30.19	33.41	35.72	37.95
18	5.62	6.26	7.01	8.23	9.39	10.86	25.99	28.87	31.53	34.81	37.16	39.42
19	6.17	6.84	7.63	8.91	10.12	11.65	27.20	30.14	32.85	36.19	38.58	40.88
20	6.72	7.43	8.26	9.59	10.85	12.44	28.41	31.41	34.17	37.57	40.00	42.34
21	7.29	8.03	8.90	10.28	11.59	13.24	29.62	32.67	35.48	38.93	41.40	43.78
22	7.86	8.64	9.54	10.98	12.34	14.04	30.81	33.92	36.78	40.29	42.80	45.20
23	8.45	9.26	10.20	11.69	13.09	14.85	32.01	35.17	38.08	41.64	44.18	46.62
24	9.04	9.89	10.86	12.40	13.85	15.66	33.20	36.42	39.36	42.98	45.56	48.03
25	9.65	10.52	11.52	13.12	14.61	16.47	34.38	37.65	40.65	44.31	46.93	49.44
26	10.26	11.16	12.20	13.84	15.38	17.29	35.56	38.89	41.92	45.64	48.29	50.83
27	10.87	11.81	12.88	14.57	16.15	18.11	36.74	40.11	43.19	46.96	49.64	52.22
28	11.50	12.46	13.56	15.31	16.93	18.94	37.92	41.34	44.46	48.28	50.99	53.59
29	12.13	13.12	14.26	16.05	17.71	19.77	39.09	42.56	45.72	49.59	52.34	54.97
30	12.76	13.79	14.95	16.79	18.49	20.60	40.26	43.77	46.98	50.89	53.67	56.33

Table G.3 (Continued) — Quantiles of chi-square

Degrees of Freedom	Lower Tail Probability											
	0.0025	0.0050	0.0100	0.0250	0.0500	0.1000	0.9000	0.9500	0.9750	0.9900	0.9950	0.9975
31	13.41	14.46	15.66	17.54	19.28	21.43	41.42	44.a99	48.23	52.19	55.00	57.69
32	14.06	15.13	16.36	18.29	20.07	22.27	42.58	46.19	49.48	53.49	56.33	59.05
33	14.71	15.82	17.07	19.05	20.87	23.11	43.75	47.40	50.73	54.78	57.65	60.39
34	15.37	16.50	17.79	19.81	21.66	23.95	44.90	48.60	51.97	56.06	58.96	61.74
35	16.03	17.19	18.51	20.57	22.47	24.80	46.06	49.80	53.20	57.34	60.27	63.08
36	16.70	17.89	19.23	21.34	23.27	25.64	47.21	51.00	54.44	58.62	61.58	64.41
37	17.37	18.59	19.96	22.11	24.07	26.49	48.36	52.19	55.67	59.89	62.88	65.74
38	18.05	19.29	20.69	22.88	24.88	27.34	49.51	53.38	56.90	61.16	64.18	67.06
39	18.73	20.00	21.43	23.65	25.70	28.20	50.66	54.57	58.12	62.43	65.48	68.38
40	19.42	20.71	22.16	24.43	26.51	29.05	51.81	55.76	59.34	63.69	66.77	69.70
41	20.11	21.42	22.91	25.21	27.33	29.91	52.95	56.94	60.56	64.95	68.05	71.01
42	20.80	22.14	23.65	26.00	28.14	30.77	54.09	58.12	61.78	66.21	69.34	72.32
43	21.50	22.86	24.40	26.79	28.96	31.63	55.23	59.30	62.99	67.46	70.62	73.62
44	22.20	23.58	25.15	27.57	29.79	32.49	56.37	60.48	64.20	68.71	71.89	74.93
45	22.90	24.31	25.90	28.37	30.61	33.35	57.51	61.66	65.41	69.96	73.17	76.22
46	23.61	25.04	26.66	29.16	31.44	34.22	58.64	62.83	66.62	71.20	74.44	77.52
47	24.32	25.77	27.42	29.96	32.27	35.08	59.77	64.00	67.82	72.44	75.70	78.81
48	25.03	26.51	28.18	30.75	33.10	35.95	60.91	65.17	69.02	73.68	76.97	80.10
49	25.74	27.25	28.94	31.55	33.93	36.82	62.04	66.34	70.22	74.92	78.23	81.38
50	26.46	27.99	29.71	32.36	34.76	37.69	63.17	67.50	71.42	76.15	79.49	82.66
60	33.79	35.53	37.48	40.48	43.19	46.46	74.40	79.08	83.30	88.38	91.95	95.34
70	41.33	43.28	45.44	48.76	51.74	55.33	85.53	90.53	95.02	100.43	104.21	107.81
80	49.04	51.17	53.54	57.15	60.39	64.28	96.58	101.88	106.63	112.33	116.32	120.10
90	56.89	59.20	61.75	65.65	69.13	73.29	107.57	113.15	118.14	124.12	128.30	132.26
100	64.86	67.33	70.06	74.22	77.93	82.36	118.50	124.34	129.56	135.81	140.17	144.29
150	105.94	109.14	112.67	117.98	122.69	128.28	172.58	179.58	185.80	193.21	198.36	203.21
200	148.43	152.24	156.43	162.73	168.28	174.84	226.02	233.99	241.06	249.45	255.26	260.74
300	235.81	240.66	245.97	253.91	260.88	269.07	331.79	341.40	349.87	359.91	366.84	373.35
400	325.18	330.90	337.16	346.48	354.64	364.21	436.65	447.63	457.31	468.72	476.61	483.99
500	415.81	422.30	429.39	439.94	449.15	459.93	540.93	553.13	563.85	576.49	585.21	593.36

Table G.4 — Critical values for the nonrandomized exact test

	α = 0.01					α = 0.05				
	t_B / t_S					t_B / t_S				
N_B	1	2	3	4	5	1	2	3	4	5
0	6	4	3	2	2	4	2	2	1	1
1	9	5	4	3	3	6	3	3	2	2
2	11	6	5	4	3	8	4	3	3	2
3	13	7	5	5	4	9	5	4	3	3
4	14	8	6	5	4	11	6	4	4	3
5	16	9	7	6	5	12	7	5	4	3
6	18	10	8	6	5	14	8	6	5	4
7	19	11	8	7	6	15	8	6	5	4
8	21	12	9	7	6	17	9	7	5	5
9	23	13	9	8	7	18	10	7	6	5
10	24	14	10	8	7	19	11	8	6	5
11	26	14	10	8	7	21	11	8	7	6
12	27	15	11	9	8	22	12	9	7	6
13	28	16	12	9	8	23	13	9	7	6
14	30	17	12	10	8	25	14	10	8	6
15	31	17	13	10	9	26	14	10	8	7
16	33	18	13	11	9	27	15	11	8	7
17	34	19	14	11	9	29	16	11	9	7
18	35	20	14	11	10	30	16	12	9	8
19	37	20	15	12	10	31	17	12	9	8
20	38	21	15	12	10	32	18	12	10	8
21	40	22	16	13	11	34	18	13	10	9
22	41	23	16	13	11	35	19	13	11	9
23	42	23	17	13	11	36	19	14	11	9
24	44	24	17	14	12	37	20	14	11	9
25	45	25	18	14	12	39	21	15	12	10
26	46	25	18	15	12	40	21	15	12	10
27	48	26	19	15	13	41	22	16	12	10
28	49	27	19	15	13	42	23	16	13	10
29	50	27	20	16	13	44	23	16	13	11
30	51	28	20	16	13	45	24	17	13	11

Table G.4 (Continued) — Critical values for the nonrandomized exact test

	α = 0.01					α = 0.05				
	t_B / t_S					t_B / t_S				
N_B	1	2	3	4	5	1	2	3	4	5
31	53	29	21	16	14	46	25	17	14	11
32	54	29	21	17	14	47	25	18	14	12
33	55	30	22	17	14	48	26	18	14	12
34	57	31	22	17	15	50	26	19	15	12
35	58	32	22	18	15	51	27	19	15	12
36	59	32	23	18	15	52	28	19	15	13
37	60	33	23	19	16	53	28	20	16	13
38	62	33	24	19	16	54	29	20	16	13
39	63	34	24	19	16	56	30	21	16	13
40	64	35	25	20	16	57	30	21	17	14
41	65	35	25	20	17	58	31	22	17	14
42	67	36	26	20	17	59	31	22	17	14
43	68	37	26	21	17	60	32	22	17	14
44	69	37	27	21	18	61	33	23	18	15
45	70	38	27	21	18	63	33	23	18	15
46	72	39	27	22	18	64	34	24	18	15
47	73	39	28	22	18	65	34	24	19	16
48	74	40	28	22	19	66	35	24	19	16
49	75	41	29	23	19	67	36	25	19	16
50	77	41	29	23	19	68	36	25	20	16
51	78	42	30	23	20	70	37	26	20	17
52	79	43	30	24	20	71	37	26	20	17
53	80	43	31	24	20	72	38	26	21	17
54	82	44	31	24	20	73	39	27	21	17
55	83	45	31	25	21	74	39	27	21	18
56	84	45	32	25	21	75	40	28	22	18
57	85	46	32	25	21	77	40	28	22	18
58	86	46	33	26	22	78	41	29	22	18
59	88	47	33	26	22	79	42	29	23	19
60	89	48	34	26	22	80	42	29	23	19

Table G.4 (Continued) — Critical values for the nonrandomized exact test

	α = 0.01					α = 0.05				
	t_B / t_S					t_B / t_S				
N_B	1	2	3	4	5	1	2	3	4	5
61	90	48	34	27	22	81	43	30	23	19
62	91	49	34	27	23	82	43	30	23	19
63	92	50	35	27	23	83	44	31	24	20
64	94	50	35	28	23	85	45	31	24	20
65	95	51	36	28	23	86	45	31	24	20
66	96	51	36	28	24	87	46	32	25	20
67	97	52	37	29	24	88	46	32	25	21
68	98	53	37	29	24	89	47	33	25	21
69	100	53	37	29	25	90	47	33	26	21
70	101	54	38	30	25	91	48	33	26	21
71	102	55	38	30	25	93	49	34	26	22
72	103	55	39	30	25	94	49	34	26	22
73	104	56	39	31	26	95	50	35	27	22
74	106	56	40	31	26	96	50	35	27	22
75	107	57	40	31	26	97	51	35	27	23
76	108	58	40	32	26	98	52	36	28	23
77	109	58	41	32	27	99	52	36	28	23
78	110	59	41	32	27	100	53	37	28	23
79	112	59	42	33	27	102	53	37	29	24
80	113	60	42	33	27	103	54	37	29	24
81	114	61	43	33	28	104	54	38	29	24
82	115	61	43	34	28	105	55	38	30	24
83	116	62	43	34	28	106	56	38	30	25
84	118	63	44	34	28	107	56	39	30	25
85	119	63	44	35	29	108	57	39	30	25
86	120	64	45	35	29	110	57	40	31	25
87	121	64	45	35	29	111	58	40	31	26
88	122	65	45	36	30	112	58	40	31	26
89	123	66	46	36	30	113	59	41	32	26
90	125	66	46	36	30	114	60	41	32	26

Table G.4 (Continued) — Critical values for the nonrandomized exact test

	α = 0.01					α = 0.05				
	t_B / t_S					t_B / t_S				
N_B	1	2	3	4	5	1	2	3	4	5
91	126	67	47	37	30	115	60	42	32	26
92	127	67	47	37	31	116	61	42	33	27
93	128	68	48	37	31	117	61	42	33	27
94	129	69	48	37	31	118	62	43	33	27
95	130	69	48	38	31	120	62	43	33	27
96	132	70	49	38	32	121	63	44	34	28
97	133	70	49	38	32	122	64	44	34	28
98	134	71	50	39	32	123	64	44	34	28
99	135	72	50	39	32	124	65	45	35	28
100	136	72	50	39	33	125	65	45	35	29
101	137	73	51	40	33	126	66	46	35	29
102	139	73	51	40	33	127	66	46	35	29
103	140	74	52	40	33	129	67	46	36	29
104	141	75	52	41	34	130	68	47	36	30
105	142	75	52	41	34	131	68	47	36	30
106	143	76	53	41	34	132	69	47	37	30
107	144	76	53	42	34	133	69	48	37	30
108	146	77	54	42	35	134	70	48	37	31
109	147	78	54	42	35	135	70	49	38	31
110	148	78	55	43	35	136	71	49	38	31
111	149	79	55	43	35	137	72	49	38	31
112	150	79	55	43	36	139	72	50	38	32
113	151	80	56	43	36	140	73	50	39	32
114	152	81	56	44	36	141	73	51	39	32
115	154	81	57	44	36	142	74	51	39	32
116	155	82	57	44	37	143	74	51	40	32
117	156	82	57	45	37	144	75	52	40	33
118	157	83	58	45	37	145	76	52	40	33
119	158	84	58	45	37	146	76	52	40	33
120	159	84	59	46	38	147	77	53	41	33

Table G.5 — Summary of probability distributions

Distribution	Parameters	Values	Probability Function	Mean	Standard Deviation
Binomial	N, p	$k = 0, 1, 2, \ldots, N$	$\binom{N}{k} p^k (1-p)^{N-k}$	Np	$\sqrt{Np(1-p)}$
Poisson	λ	$k = 0, 1, 2, 3, \ldots$	$\frac{\lambda^k e^{-\lambda}}{k!}$	λ	$\sqrt{\lambda}$
Rectangular	$a_-,\ a_+$ $a = \frac{a_+ - a_-}{2}$	$x \in [a_-, a_+]$	$\frac{1}{a_+ - a_-}$	$\frac{a_- + a_+}{2}$	$\frac{a}{\sqrt{3}}$
Triangular	a_-, a_+ $a = \frac{a_+ - a_-}{2}$	$x \in [a_-, a_+]$	$\begin{cases} \frac{x - a_-}{a^2}, & x \le \frac{a_- + a_+}{2} \\ \frac{a_+ - x}{a^2}, & x \ge \frac{a_- + a_+}{2} \end{cases}$	$\frac{a_- + a_+}{2}$	$\frac{a}{\sqrt{6}}$
Trapezoidal	$a_-,\ a_+, \beta$ $a = \frac{a_+ - a_-}{2}$	$x \in [a_-, a_+]$	$\begin{cases} \frac{x - a_-}{a^2(1-\beta^2)}, & x \le \frac{a_- + a_+}{2} - a\beta \\ \frac{1}{a(1+\beta)}, & \left\lvert x - \frac{a_- + a_+}{2} \right\rvert \le a\beta \\ \frac{a_+ - x}{a^2(1-\beta^2)}, & x \ge \frac{a_- + a_+}{2} + a\beta \end{cases}$	$\frac{a_- + a_+}{2}$	$a\sqrt{\frac{1+\beta^2}{6}}$
Normal	μ, σ	$x \in (-\infty, \infty)$	$\frac{1}{\sigma\sqrt{2\pi}} e^{-(x-\mu)^2/2\sigma^2}$	μ	σ
Log-Normal	$\mu_g,\ \sigma_g$	$x \in (0, \infty)$	$\frac{\exp\left(-\ln(x/\mu_g)^2 / 2(\ln\sigma_g)^2\right)}{x(\ln\sigma_g)\sqrt{2\pi}}$	$\mu_g e^{(\ln\sigma_g)^2/2}$	$\mu_g\sqrt{e^{2(\ln\sigma_g)^2} - e^{(\ln\sigma_g)^2}}$
Student's t	ν	$x \in (-\infty, \infty)$	$\frac{\Gamma((\nu+1)/2)}{\Gamma(\nu/2)\sqrt{\nu\pi}} \left(1 + \frac{x^2}{\nu}\right)^{-(\nu+1)/2}$	$0 \quad (\nu > 1)$	$\sqrt{\frac{\nu}{\nu-2}} \quad (\nu > 2)$
Exponential	λ	$x \in [0, \infty)$	$\lambda e^{-\lambda x}$	$\frac{1}{\lambda}$	$\frac{1}{\lambda}$
Chi-Square	ν	$x \in [0, \infty)$	$\frac{x^{\nu/2-1} e^{-x/2}}{2^{\nu/2}\Gamma(\nu/2)}$	ν	$\sqrt{2\nu}$

$\Gamma(x)$ denotes the gamma function. $\Gamma(1/2) = \sqrt{\pi}$, $\Gamma(1) = 1$, and $\Gamma(x+1) = x \cdot \Gamma(x)$ for $x > 0$.

GLOSSARY

absorption **(10.3.2):** The uptake of particles of a gas or liquid by a solid or liquid, or uptake of particles of a liquid by a solid, and retention of the material throughout the external and internal structure of the uptaking material. Compare with *adsorption*.

abundance **(16.2.2):** See *emission probability per decay event*.

accreditation **(4.5.3, Table 4.2):** A process by which an agency or organization evaluates and recognizes a program of study or an institution as meeting certain predetermined qualifications or standards through activities which may include performance testing, written examinations or facility audits. *Accreditation* may be performed by an independent organization, or a federal, state, or local authority. *Accreditation* is acknowledged by the accrediting organizations issuing of permits, licences, or certificates.

accuracy **(1.4.8*)*:** The closeness of a measured result to the true value of the quantity being measured. Various recognized authorities have given the word *accuracy* different technical definitions, expressed in terms of *bias* and *imprecision*. MARLAP avoids all of these technical definitions and uses the term "accuracy" in its common, ordinary sense, which is consistent with its definition in ISO (1993a).

acquisition strategy options **(2.5, Table 2.1):** Alternative ways to collect needed data.

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)*.

activity, chemical **(*a*) (10.3.5):** (1) A thermodynamic quantity used in place of molal concentration in equilibrium expressions for reactions of real (nonideal) solutions. Activity indicates the actual behavior of *ions* in solution as a result of their interactions with the *solvent* and with each other. *Ions* deviate from ideal behavior as their concentration in solution increases and are not as effective in their chemical and physical behavior as their molar concentration would indicate. Thus, their effective concentration, a, is less than their stoichiometric concentration, c. (2) A measure of the effective molal concentration, c, in moles/Kg, of an *ion* under real (nonideal) solution conditions.

( ) *Indicates the section in which the term is first used in MARLAP.*
Italicized words or phrases have their own definitions in this glossary.

***activity, of radionuclides* (*A*) (2.5.4.1):** Mean rate of nuclear decay occurring in a given quantity of material.

***activity coefficient* (*γ*) (14.6.1):** (1) A fractional number that represents the extent that *ions* deviate from ideal behavior in solution (see *activity, chemical*). The *activity coefficient* multiplied times the molal concentration of *ions* in solution equals the chemical *activity*: $a = \gamma \cdot c$, where $\gamma \leq 1$; thus, the *activity coefficient* is a correction factor applied to molal concentrations. At infinite dilution where behavior is ideal, $\gamma = 1.0$, but it decreases as the concentration of *ions* increases. (2) The ratio of effective (apparent) concentration of an *ion* in solution to the stoichiometric concentration, $\gamma = a/c$.

***adsorption* (6.5.1.1):** Uptake of particles of a gas, liquid, or solid onto the surface of another substance, usually a solid. Compare with *absorption*.

***adsorption chromatography* (14.7.1):** A chromatographic method that partitions (separates) components of a mixture through their different adsorption characteristics on a stationary solid phase and their different solubilities in a mobile liquid phase.

***affinity chromatography* (14.7.1):** A chromatographic method that partitions (separates) proteins and nucleic acids in a mobile phase based on highly selective, very specific complementary bonds with antibody groups (*ligands*) that are chemically bonded to an inert solid matrix acting as the *stationary phase*.

***aliquant* (3.3.1.2):** 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.

***alternate analyte* (2.5):** *Analyte* whose concentration, because of an established relationship (e.g., secular equilibrium) can be used to quantitatively determine the concentration of a *target analyte*. An *alternate analyte* may be selected for analysis in place of a *target analyte* because of ease of analysis, lower analytical costs, better methodologies available, etc. (see *alternate radionuclide*).

***alternate radionuclide* (3.3.4):** An "easy-to-measure" *radionuclide* that is used to estimate the amount of a radionuclide that is more difficult or costly to measure. Known or expected relationships between the radionuclide and its alternate can be used to establish a factor for amount of the hard-to-measure radionuclide (see *alternate analyte*).

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Italicized words or phrases have their own definitions in this glossary.

***alternative hypothesis* (H_1 *or* H_A) (2.5, Table 2.1):** One of two mutually exclusive statements tested in a statistical hypothesis test (compare with *null hypothesis*). The *null hypothesis* is presumed to be true unless the test provides sufficient evidence to the contrary, in which case the *null hypothesis* is rejected and the *alternative hypothesis* is accepted.

***analyte* (1.4.7):** The component (e.g., a *radionuclide* or chemical compound) for which a *sample* is analyzed.

***analysis* (3.3.1):** Analysis refers to the identification or quantification process for determining a *radionuclide* in a *radionuclide*/matrix combination. Examples of analyses are the measurement of ^{3}H in water, ^{90}Sr in milk, ^{239}Pu in soil, etc.

***analytical data requirements* (1.1):** Measurement performance criteria used to select and decide how the laboratory analyses will be conducted and used for the initial, ongoing, and final evaluation of the laboratory's performance and the laboratory data. The project-specific *analytical data requirements* establish measurement performance criteria and decisions on how the laboratory analyses will be conducted (e.g., method selection, etc.) in a *performance-based approach* to data quality.

***analytical method* (1.4.6):** A major component of an analytical protocol that normally includes written procedures for sample digestion, chemical separation (if required), and counting (*analyte* quantification through radioactive decay emission or atom-counting measurement techniques. Also called *laboratory method*.

***analytical performance measure* (2.3.3):** A qualitative or quantitative aspect of the analysis, initially defined based on the *analyte*, its desired detection level and the sample matrix. See also *measurement quality objectives*.

***analytical plan* (9.6.3):** The portion of the *project plan documents* that addresses the optimized analytical design and other analytical issues (e.g., *analytical protocol specifications*, *standard operating procedures*).

***analytical process* (1.3):** The *analytical process* is a general term used by MARLAP to refer to a compilation of actions starting from the time a *sample* is collected and ending with the reporting of data. These are the actions that must be accomplished once a sample is collected in order to produce analytical data. These actions typically include field sample preparation and preservation, sample receipt and inspection, laboratory sample preparation, *sample dissolution*, *chemical separations*, preparation of samples for instrument measurements, instrument measurements, data reduction, data reporting, and the *quality control* of the process.

( ) *Indicates the section in which the term is first used in MARLAP.*
Italicized words or phrases have their own definitions in this glossary.

***analytical protocol* (1.4.3):** A compilation of specific procedures/methods that are performed in succession for a particular analytical process. With a performance-based approach, there may be a number of appropriate analytical protocols for a particular analytical process. The *analytical protocol* is generally more inclusive of the activities that make up the analytical process than is the *analytical method*. See also *analytical process*.

***analytical protocol specification* (*APS*) (1.4.10):** The output of a *directed planning process* that contains the project's analytical data needs and requirements in an organized, concise form. The level of specificity in the APSs should be limited to those requirements that are considered essential to meeting the project's *analytical data requirements* to allow the laboratory the flexibility of selecting the protocols or methods that meet the analytical requirements.

***anion* (13.2.2):** An *ion* with a negative charge.

***anion exchanger* (14.7.4.2):** An ion-exchange *resin* consisting of chemical groups, bonded to an inert matrix, with a net positive charge. The positive species are electrostatically bonded to negative, labile *ions* bonded to an inert matrix. *Anions* in solution replace the labile *ions* on the exchanger by forming electrostatic bonds with the charged groups. The strength of attraction, which depends on the charge, size, and degree of solvation of the *anion*, provides a means for separating *analyte ions*.

***aqueous samples* (10.3.1):** Samples for which the matrix is water, including surface water, groundwater, drinking water, precipitation, or runoff.

***arithmetic mean* ($\bar{x}$) (1.4.8):** The sum of a series of measured values, divided by the number of values. The *arithmetic mean* is also called the "average." If the measured values are denoted by $x_1, x_2, \ldots, x_N$, the *arithmetic mean* is equal to $(x_1 + x_2 + \cdots + x_N) / N$. (See also *expectation* and *sample mean*.)

***assessment team* (9.4):** A team of data assessors (or qualified data assessor) who are technically competent to evaluate the project's activities and the impact of these activities on the quality and usability of data.

***audit* (5.3.8):** An assessment to provide assurance that a selected laboratory is capable of or is fulfilling the specifications of the *request for proposals* or *statement of work*. A pre-award *audit* verifies that a laboratory has the ability that it can meet the analytical requirements of the *request for proposals* or *statement of work*. After the award, an *audit* of a laboratory will assess the performance of the laboratory to verify that it is complying with *statement of work* and

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contractual requirements. Thus, the examination of logbooks, charts, or other documentation that are produced as the work progresses.

***authoritative sample collection approach* (9.6.2.1):** An approach wherein professional knowledge is used to choose sample locations and times.

***auto-oxidation-reduction (disproportionation)* (14.2.3):** An *oxidation-reduction reaction* in which a single chemical species acts simultaneously as an oxidizing and reducing agent.

***average* (6.5.1.1):** See *arithmetic mean*.

***background, anthropogenic* (3.3.1):** Background radiation levels caused by *radionuclides* in the environment resulting from human activities, such as the atmospheric testing of nuclear weapons.

***background, environmental* (3.3.1):** See *background level*. The presence of naturally occurring radiation or *radionuclides* in the environment.

***background, instrument* (6.5.5.3):** Radiation detected by an instrument when no *source* is present. The background radiation that is detected may come from *radionuclides* in the materials of construction of the detector, its housing, its electronics and the building as well as the environment and natural radiation.

***background level* (2.5):** This term usually refers to the presence of *radioactivity* or radiation in the environment. From an analytical perspective, the presence of background *radioactivity* in samples needs to be considered when clarifying the radioanalytical aspects of the decision or study question. Many *radionuclides* are present in measurable quantities in the environment. Natural background radiation is due to both primordial and *cosmogenic radionuclides*. Anthropogenic background is due to *radionuclides* that are in the environment as a result of human activities, for example, the atmospheric testing of nuclear weapons.

***basic ordering agreement* (*BOA*) (5.1):** A process that serves to pre-certify potential analytical service providers. A list of approved laboratories is assembled and contacted as needed to support specific needs. A task order is used to define a specific scope of work within a BOA.

***batch processing* (6.4):** A procedure that involves preparing a group of individual samples together for analysis in such a way that allows the group to be associated with a set of *quality control samples*.

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***becquerel* (*Bq*) (1.4.9):** Special name for the SI derived unit of activity (of *radionuclides*), equal to one nuclear transformation per second. The traditional unit is the *curie (Ci)*. The relationship between these units is 3.7×10^{10} Bq = 1 Ci.

***bias (of an estimator)* (1.4.8):** If X is an estimator for the true value of parameter θ, then the *bias* of X is $\mu_X - \theta$, where μ_X denotes the expectation of X.

***bias (of measurement)* (1.4.8):** See *systematic error*.

***bias (of a measurement process)* (1.4.8):** The *bias* of a measurement process is a persistent deviation of the mean measured result from the true or accepted reference value of the quantity being measured, which does not vary if a measurement is repeated. See also *bias (of an estimator)* and *bias (of measurement)*.

***bioassay* (10.2.11.2):** A procedure to monitor internal radiation exposure by performing *in vitro* or *in vivo* measurements, primarily urine analysis, fecal analysis, or whole-body counting.

***blind sample* (18.4.2):** A *sample* whose concentration is not known to the analyst. *Blind samples* are used to assess analytical performance. A double-blind sample is a *sample* whose concentration and identity as a *sample* is known to the submitter but not to the analyst. The double-blind sample should be treated as a routine sample by the analyst, so it is important that the double-blind sample is identical in appearance to routine samples.

***blunder* (7.4.1.1):** A mistake made by a person performing an analytical task that produces an a significant error in the result.

***branching ratio* (7.2.2.2):** See *emission probability per decay event*.

***breakthrough* (14.7.4.1):** Appearance of certain *ions* in the output solution (*eluate*) of an ion-exchange column. These *ions* are not bonded to the exchange groups of the column because the groups are already occupied by these or other *ions*, and the *resin* is essentially saturated.

***calibration* (1.4.8):** The set of operations that establish, under specified conditions, the relationship between values indicated by a measuring instrument or measuring system, or values represented by a material measure, and the corresponding known value of a *measurand*.

***calibration source* (15.1):** A prepared *source*, made from a *certified reference material* (standard), that is used for calibrating instruments.

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***carrier* (14.1):** (1) A stable isotopic form of a tracer element or nonisotopic material added to effectively increase the quantity of a tracer element during radiochemical procedures, ensuring conventional behavior of the element in solution. (2) A substance in appreciable amount that, when associated with a tracer of a specified substance, will carry the tracer with it through a chemical or physical process, or prevent the tracer from undergoing nonspecific processes due to its low concentration (IUPAC, 1995). A stable isotope of a *radionuclide* (usually the *analyte*) added to increase the total amount of that element so that a measurable mass of the element is present.

***carrier-free tracer* (14.2.6):** (1) A radioactive isotope tracer that is essentially free from stable (nonradioactive) isotopes of the element in question. (2) Addition of a specific, nonradioactive isotope of an element to change the measured isotopic abundance of the element in the *sample*. Such materials are usually designated as nonisotopic material or marked with the symbol "c.f." (see *radiotracer*).

***carrier gas* (14.5.1):** An inert gas, such as nitrogen or helium, serving as the mobile phase in a gas-liquid chromatographic system. The *carrier gas* sweeps the *sample* in through the system.

***cation* (13.2.2):** An *ion* with a positive charge.

***cation exchanger* (14.3.4.2):** An ion-exchange *resin* consisting of chemical groups, bonded to an inert matrix, with a net negative charge. The negative species are electrostatically bonded to positive, labile *ions*. Cations, in solution, replace the labile *ions* on the exchanger by forming electrostatic bonds with the charged groups. The strength of attraction, which depends on the charge, size, and degree of solvation of the cation, provides a means for separating *analyte ions*.

***Cerenkov radiation* (14.10.9.10):** Cerenkov radiation is emitted in the ultraviolet spectrum when a fast charged particle traverses a dielectric medium (like water) at a velocity exceeding the velocity of light in that medium. It is analogous to the "sonic boom" generated by a craft exceeding the speed of sound.

***certified reference material* (*CRM*) (1.6, Figure 1.3):** A reference material, accompanied by a certificate, one or more of whose property values are certified by a procedure which establishes its traceability to an accurate realization of the unit in which the property values are expressed, and for which each certified value is accompanied by an uncertainty at a stated level of confidence (ISO, 1992).

***chain-of-custody* (1.4.10):** Procedures that provide the means to trace the possession and handling of a *sample* from collection to data reporting.

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***check source* (15.2):** A material used to validate the operability of a radiation measurement device, sometimes used for instrument *quality control*. See *calibration source*, *test source*, and *source, radioactive*.

***chelate* (14.3.2):** A *complex ion* or compound that consists of a *ligand* bonded (coordinated) to a metal atom or *ion* through two or more nonmetal atoms forming a ring structure with the metal atom or *ion*. *Ligands* may be inorganic *ions*, such as Cl, F, or carbonate, or organic compounds of two, four, or six functional groups containing atoms of S, N, O, or P.

***chelating agent* (14.3.2):** The compound containing the *ligand* that forms a chelate with metal atoms or *ions*.

***chemical separations* (1.1):** The removal of all undesirable materials (elements, compounds, etc.) from a *sample* through chemical means so that only the intended *analyte* is isolated and measured.

***chemical speciation* (2.5):** The chemical state or form of an *analyte* in a *sample*. When the chemical species of the *analyte* in a *sample* from a new project varies from the chemical species for which an *analytical method* was validated, then the method should be altered and revalidated.

***chromatography* (6.6.3.4):** A group of separation techniques based on the unequal distribution (partition) of substances between two immiscible phases, one moving past the other. The mobile phase passes over the surfaces of the *stationary phase*.

***coagulation* (14.8.5):** (1) The process in which colloidal particles or macromolecules come together to form larger masses (see *colloid* and *colloidal solution*). (2) Addition of an excess quantity of electrolyte to a *colloidal solution* neutralizing the electrical bilayer of the colloidal particles and permitting their agglomeration to form larger particles that easily settle (precipitate). Also called “flocculation.”

***coefficient of variation* (*CV*) (19.5.2.2):** The *coefficient of variation* of a nonnegative random variable is the ratio of its *standard deviation* to its *mean*.

***coefficient of thermal (volume) expansion* (19E.3):** ratio of the change in volume (of a material) per unit volume to the change in temperature, at constant pressure. If V denotes volume, ρ denotes density, and T denotes temperature, then the coefficient of thermal expansion, β, is given by

$$\beta = \frac{1}{V}\frac{dV}{dT} = -\frac{1}{\rho}\frac{d\rho}{dT}.$$

***collectors* (14.8.5):** Substances used for the unspecific concentration of trace substances. Colloidal precipitates are excellent collectors because of their great adsorption capacity. Unspecific *carriers* such as manganese dioxide, sulfides, and hydrated oxides are frequently used as *collectors* (also called "scavengers").

***colloid* (13.2.5):** Any form of matter with at least one dimension that is less than one micron but more than one nanometer. This dimension is larger in size than that of a true solution but smaller than particles of an ordinary suspension. They are too small to be observed by a light microscope but larger than molecular size. Colloidal particles are usually aggregates of hundreds or thousands of smaller molecules or macromolecules.

***colloidal solution* (13.4.1):** Sometimes called a "colloidal dispersion." (1) A mixture formed from the dispersion of one phase (dispersed phase) within a second phase (continuous phase) in which one phase has colloidal dimensions. A *colloidal solution* contains dispersed particles with a very high surface-area-to-mass ratio and, thus, a great adsorption capacity. The solution will not usually settle by gravity since the colloidal particles are very small and charged by attraction of *ions* to their surfaces, but they will pass through ordinary filter paper. (2) In radiochemistry, a *colloidal solution* refers to the dispersion of solid particles in the solution phase. (*The mixture is not a true solution because particles of the dispersed phase are larger than typical ions and molecules.*)

***column chromatography* (14.3.4.2):** A chromatographic procedure employing a solid phase packed in a glass or metal column. A liquid phase is passed through the column under pressure supplied by gravity or pumping action. Column chromatography can accommodate larger quantities of materials than other methods of chromatography and, thus, can separate larger loads. It can also provide more separating power with an increased ratio of solid phase to *analyte*.

***combined standard uncertainty* (1.4.7):** *Standard uncertainty* of an *output estimate* calculated by combining the standard uncertainties of the *input estimates*. See also *expanded uncertainty and uncertainty (of measurement)*. The *combined standard uncertainty* of y is denoted by $u_c(y)$.

***combined variance* (19.3.3):** The square of the *combined standard uncertainty*. The *combined variance* of y is denoted by $u^2_c(y)$.

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***committed effective dose equivalent* (*CEDE*) (2.5.2.1):** The sum of the committed dose equivalent to various tissues in the body, each multiplied by the appropriate weighting factor (MARSSIM, 2000). CEDE is expressed in units of sievert (Sv) or rem. See *action level*, *dose equivalent*, and *total effective dose equivalent*.

***common ion* (14.8.3.1):** *Ions* that appear in the equilibrium expressions of reactions. The term is often used to refer to an additional source of the reacting *ions*.

***common-ion effect* (14.8.3.1):** An increase in concentration of *ions* participating in a reaction because of the addition of one of the *ions* from another source causing a shift in the equilibrium of the reaction.

***comparability* (1.4.11):** A measure of the confidence with which one data set can be compared to another. *Comparability* is one of the five principal *data quality indicators*, which are qualitative and quantitative descriptors used in interpreting the degree of acceptability or utility of data.

***completeness* (1.4.11):** A measure of the amount of valid data obtained from a measurement system compared to the amount that was expected to be obtained under correct, normal conditions. *Completeness* is one of the five principal *data quality indicators*. See also *comparability*.

***complex* (13.2.4):** Another name for a *coordination compound*.

***complex ion* (13.2.4):** An *ion* formed when a metal atom or *ion* forms *coordination bonds* with one or more nonmetal atoms in molecules or *anions*. Examples are $Th(NO_3)_2^{+2}$, $Ra(EDTA)^{-2}$, $U(CO_3)_5^{-6}$, and $Fe(H_2O)_6^{+2}$.

***compliance* (8.2.2.2):** In terms of data, *compliance* means that the data passes numerical *quality control tests* based on parameters or limits derived from the *measurement quality objectives* specified in the *statement of work*.

***component (of combined standard uncertainty)* (19.2):** The *component* of the comb*ined standard uncertainty* of an output estimate, $u_c(y)$, generated by the *standard uncertainty* of an input estimate, $u(x_i)$, is the product of the *standard uncertainty*, $u(x_i)$, and the absolute value of the *sensitivity coefficient*, $\partial y / \partial x_i$. The uncertainty component generated by $u(x_i)$ may be denoted by $u_i(y)$.

***concentration range* (2.5, Table 2.1):** The minimum and maximum concentration of an *analyte* expected to be present in a *sample* for a given project. While most analytical protocols are

applicable over a fairly large range of concentration for the *radionuclide of interest*, performance over a required concentration range can serve as a measurement quality objective for the protocol selection process and some analytical protocols may be eliminated if they cannot accommodate the expected range of concentration.

***conceptual site model* (2.3.2):** A general approach to planning field investigations that is useful for any type of environmental reconnaissance or investigation plan with a primary focus on the surface and subsurface environment.

***consistency* (8.4.2):** Values that are the same when reported redundantly on different reports or transcribed from one report to another.

***control chart* (18.1):** A graphical representation of data taken from a repetitive measurement or process. *Control charts* may be developed for various characteristics (e.g., *mean*, *standard deviation*, range, etc.) of the data. A *control chart* has two basic uses: 1) as a tool to judge if a process was *in control*, and 2) as an aid in achieving and maintaining *statistical control*. For applications related to radiation detection instrumentation or radiochemical processes, the *mean* (center line) value of a historical characteristic (e.g., *mean* detector response), subsequent data values and *control limits* placed symmetrically above and below the center line are displayed on a *control chart*. See *statistical control*.

***control limit* (3.3.7.3):** Predetermined values, usually plotted on a *control chart*, which define the acceptable range of the monitored variable. There can be both upper and lower limits; however, when changes in only one direction are of concern, only one limit is necessary. When a measured value exceeds the control limits, one must stop the measurement process, investigate the problem, and take corrective action." See *warning limit*.

***coordination bond* (14.3.1):** (1) The chemical bond between the nonmetal atoms of a *ligand* and a metal atom or *ion*, which forms a coordination compound or *complex ion*. The bond is formed when the *ligand* donates one or more electron pairs to the metal atom or *ion*. (2) In more general terms, a covalent bond formed in which one atom donates both of the shared electrons; often called a coordination-covalent bond.

***coordination compound* (14.3.1):** A compound containing *coordination bonds* in a molecule or *ion*; also called a "*complex*."

***coordination number* (14.3.1):** (1) The number of nonmetal atoms donating electrons to a metal atom or *ion* in the formation of a *complex ion* or coordination compound. For example, the

coordination number is five in $U(CO_3)_5^{-6}$ (2) The number of atoms, *ions*, molecules, or groups surrounding an atom or *ion* in a coordination compound, *complex ion*, or crystal structure.

***coprecipitation* (14.1):** A process used to precipitate a *radionuclide* that is not present in sufficient concentration to exceed the solubility product of the *radionuclide* and precipitate. A stable *ion*, chemically similar to the *radionuclide*, is added in a quantity sufficient to precipitate and carry with it the *radionuclide*.

***core group (core team)* (2.4.1):** A subgroup of the *project planning team*, which includes the project manager and other key members of the *project planning team*, who meet at agreed upon intervals to review the project's progress, respond to unexpected events, clarify questions raised, revisit and revise project requirements as necessary, and communicate the basis for previous assumptions.

***correction* (8.2.1):** A value algebraically added to the uncorrected result of a measurement to compensate for a systematic effect.

***correction factor* (8.5.1.12):** A numerical factor by which the result of an uncorrected result of a measurement is multiplied to compensate for a systematic effect.

***corrective action reports* (8.2.2.2):** Documentation of required steps taken to correct an out of control situation.

***correctness* (8.4.2):** The reported results are based on properly documented and correctly applied algorithms.

***correlate* (18.4.5):** Two *random variables* are *correlated* if their *covariance* is nonzero.

***correlation coefficient* (19.3.3):** The *correlation coefficient* of two *random variables* is equal to their *covariance* divided by the product of their *standard deviations*.

***cosmogenic radionuclide* (3.3.1):** *Radionuclides* that result from the collision of cosmic-ray particles with stable elements in the atmosphere, primarily atmospheric gases. See *background, environmental*.

***counting efficiency* (15.2.2):** The ratio of the events detected (and registered) by a radiation detection system to the number of particle or photons emitted from a radioactive *source*. The counting efficiency may be a function of many variables, such as radiation energy, *source* composition, and *source* or detector geometry.

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***counting error* (19.3.5):** See *counting uncertainty*; *error (of measurement)*. MARLAP uses the term *counting uncertainty* to maintain a clear distinction between the concepts of measurement *error* and *uncertainty*.

***counting uncertainty* (18.3.4):** Component of *measurement uncertainty* caused by the random nature of radioactive decay and radiation counting.

***count rate* (14A.2.2):** The number of decay particles detected per unit time of a *source*. Generally the *count rate* is uncorrected for detector efficiency. The *count rate* divided by the detector efficiency for a specific particle and energy will yield the *source activity*.

***count time* (2.5):** The time interval for the counting of a *sample* or *source* by a radiation detector. Depending upon the context used, this can be either the "clock" time (the entire period required to count the *sample*), or "live" time (the period during which the detector is actually counting). Live time is always less than or equal to clock time.

***covariance* (19.3.3):** The *covariance* of two *random variables X* and *Y*, denoted by Cov(*X*,*Y*) or $\sigma_{X,Y}$, is a measure of the association between them, and is defined as $E([X - \mu_X][Y - \mu_Y])$.

***coverage factor* (1.4.7):** The value *k* multiplied by the *combined standard uncertainty* $u_c(y)$ to give the *expanded uncertainty*, *U*.

***coverage probability* (19.3.6):** Approximate probability that the reported uncertainty interval will contain the value of the *measurand*.

***critical level* (20B.1):** See *critical value*.

***critical value* (S_C) (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*.

***cross-contamination* (3.4, Table 3.1):** Cross-contamination occurs when radioactive material in one *sample* is inadvertently transferred to an uncontaminated sample, which can result from using contaminated sampling equipment and chemicals, and improperly cleaned glassware, crucibles, grinders, etc. *Cross-contamination* may also occur from spills, as well as airborne dusts of contaminated materials.

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***crosstalk* (7.4.2.2):** A phenomenon in gas-proportional counting or liquid-scintillation counting when an emission of an alpha particle is recorded as a beta particle count or vice versa. This is due to the ionization effects of the particles at different energies.

***cumulative distribution function* (19A.1):** See *distribution function*.

***curie* (*Ci*) (1.4.9):** Traditional non-SI unit of activity (of *radionuclides*), equal to 3.7×10^{10} Bq. Because the curie is such a large value, the more common unit is the *picocurie* (pCi), equal to 10^{-12} Ci.

***data assessment* (2.1):** Assessment of environmental data consists of three separate and identifiable phases: data verification, data validation, and *data quality assessment*.

***data collection activities* (1.3):** Examples of *data collection activities* include site-characterization activities, site cleanup and compliance-demonstration activities, decommissioning of nuclear facilities, remedial and removal actions, effluent monitoring of licensed facilities, license termination activities, environmental site monitoring, background studies, routine ambient monitoring, and waste management activities.

***data life cycle* (1.4.1):** A useful and structured means of considering the major phases of projects that involve data collection activities. The three phases of the *data life cycle* are the planning phase, the implementation phase, and the assessment phase.

***data package* (1.4.11):** The information the laboratory should produce after processing samples so that data verification, validation, and quality assessment can be done (see Chapter 16, Section 16.7).

***data qualifier* (8.1):** *Data validation* begins with a review of project objectives and requirements, the *data verification* report, and the identified exceptions. If the system being validated is found to be *in control* and applicable to the *analyte* and matrix, then the individual data points can be evaluated in terms of detection, *imprecision*, and *bias*. The data are then assigned *data qualifiers*. Validated data are rejected only when the impact of an exception is so significant that a datum is unreliable.

***data quality assessment* (1.1):** The scientific and statistical evaluation of data to determine if data are the right type, quality, and quantity to support their intended use.

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***data quality assessment plan* (1.4.1, Figure 1.1):** A *project plan document* that describes the *data quality assessment* process including *data quality assessment* specifications, requirements, instructions, and procedures.

***data quality indicator* (*DQI*) (3.3.7):** Qualitative and quantitative descriptor used in interpreting the degree of acceptability or utility of data. The principal DQIs are *precision*, *bias*, *representativeness*, *comparability*, and *completeness*. These five DQIs are also referred to by the acronym PARCC—the "A" refers to *accuracy* rather than *bias*.

***data quality objective* (*DQO*) (1.4.9):** *DQOs* are qualitative and quantitative statements derived from the *DQO process* that clarify the study objectives, define the most appropriate type of data to collect, determine the most appropriate conditions from which to collect the data, and specify tolerable limits on *decision error rates*. Because DQOs will be used to establish the quality and quantity of data needed to support decisions, they should encompass the total uncertainty resulting from all data collection activities, including analytical and sampling activities.

***data quality objective process* (1.6.3):** A systematic strategic planning tool based on the scientific method that identifies and defines the type, quality, and quantity of data needed to satisfy a specified use. *DQOs* are the qualitative and quantitative outputs from the *DQO process*.

***data quality requirement* (2.1):** See *measurement quality objective*.

***data reduction* (1.1):** The processing of data after generation to produce a *radionuclide* concentration with the required units.

***data transcription* (8.5):** The component of the analytical process involving copying or recording data from measurement logs or instrumentation.

***data usability* (1.4.11):** The scientific and statistical evaluation of data sets to determine if data are of the right type, quality, and quantity to support their intended use (*data quality objectives*). The data quality assessor integrates the *data validation* report, field information, assessment reports, and historical project data to determine *data usability* for the intended decisions.

***data validation* (1.1):** The evaluation of data to determine the presence or absence of an *analyte* and to establish the uncertainty of the measurement process for contaminants of concern. *Data validation* qualifies the usability of each datum (after interpreting the impacts of exceptions identified during data verification) by comparing the data produced with the *measurement quality objectives* and any other *analytical process* requirements contained in the *analytical protocol specifications* developed in the planning process.

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***data validation plan* (1.4.1, Figure 1.1):** A *project plan document* that ensures that proper laboratory procedures are followed and data are reported in a format useful for validation and assessment, and will improve the cost-effectiveness of the data collection process.

***data verification* (1.2):** Assures that laboratory conditions and operations were compliant with the *statement of work*, *sampling and analysis plan*, and *quality assurance project plan*, and identifies problems, if present, that should be investigated during data validation. *Data verification* compares the material delivered by the laboratory to these requirements (compliance), and checks for consistency and *comparability* of the data throughout the data package and *completeness* of the results to ensure all necessary documentation is available.

***decay chain* (3.3.8):** A *decay chain* or "decay series" begins with a parent radionuclide (also called a "parent nuclide"). As a result of the radioactive decay process, one element is transformed into another. The newly formed element, the decay product or progeny, may itself be radioactive and eventually decay to form another nuclide. Moreover, this third decay product may be unstable and in turn decay to form a fourth, fifth or more generations of other radioactive decay products. The final decay product in the series will be a stable element. Elements with extremely long half-lives may be treated as if stable in the majority of cases. Examples of important naturally occurring *decay chains* include the uranium series, the thorium series, and the actinium series. See *radioactive equilibrium*.

***decay emissions* (6.2):** The emissions of alpha or beta particles (β^+ or β^-) or gamma rays from an atomic nucleus, which accompany a nuclear transformation from one atom to another or from a higher nuclear energy state to lower one.

***decay factor* (14A.2.2):** Also referred to as the "decay-correction factor." The factor that is used to compensate for radioactive decay of a specific *radionuclide* between two points in time.

***decay series* (3.3.4):** See *decay chain*.

***decision error rate* (1.4.9):** The probability of making a wrong decision under specified conditions. In the context of the *DQO process*, one considers two types of decision errors (*Type I* and *Type II*). The *project planning team* determines the *tolerable decision error rates*.

***decision level* (20.2.2):** See *critical value*.

***decision performance criteria* (2.1):** Another way to express the concept of using directed project planning as a tool for project management to identify and document the qualitative and quantitative statements that define the project objectives and the acceptable rate of making

decision errors that will be used as the basis for establishing the quality and quantity of data needed to support the decision. See *data quality objective*.

***decision rule* (2.3.3):** The rule developed during directed planning to get from the problem or concern to the desired decision and define the limits on the *decision error rates* that will be acceptable to the *stakeholder* or customer. Sometimes called a "decision statement." The *decision rule* can take the form of "if …then…" statements for choosing among decisions or alternative actions. For a complex problem, it may be helpful to develop a *decision tree*, arraying each element of the issue in its proper sequence along with the possible actions. The *decision rule* identifies (1) the *action level* that will be a basis for decision and (2) the statistical parameter that is to be compared to the *action level*.

***decision tree* (2.5.3):** See *decision rule.* Also referred to as a "logic flow diagram" or "decision framework."

***decision uncertainty* (1.4.7):** Refers to uncertainty in the decisionmaking process due to the probability of making a wrong decision because of measurement uncertainties and sampling statistics. *Decision uncertainty* is usually expressed as by the estimated probability of a decision error under specified assumptions.

***decommissioning* (1.3):** The process of removing a facility or site from operation, followed by decontamination, and license termination (or termination of authorization for operation) if appropriate. The process of *decommissioning* is to reduce the residual *radioactivity* in structures, materials, soils, groundwater, and other media at the site to acceptable levels based on acceptable risk, so that the site may be used without restrictions.

***deconvolution* (8.5.1.11):** The process of resolving multiple gamma-spectral peaks into individual components.

***deflocculation* (14.8.5):** The process whereby coagulated particles pass back into the colloidal state. Deflocculation may be accomplished by adding a small amount of electrolyte to produce the electrical double-layer characteristic of colloidal particles. Also called "peptization." Also see *coagulation* and *colloidal solution*.

***degrees of freedom* (6A.2):** In a statistical estimation based on a series of observations, the number of observations minus the number of parameters estimated. See *effective degrees of freedom*.

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***dentate* (14.3.1):** Term used to categorize *ligands* that describes the number of nonmetal atoms with electron pairs used by a *ligand* for coordinate bond formation (unidentate, bidentate, etc.).

***derived concentration guideline level (DCGL)* (2.5.2.1):** A derived radionuclide-specific activity concentration within a *survey unit* corresponding to the release criterion. *DCGLs* are derived from activity/dose relationships through various exposure pathway scenarios.

***descriptive statistics* (9.6.4.1):** Statistical methods that are used to determine and use the *mean*, mode, *median*, *variance*, and correlations among variables, tables, and graphs to describe a set of data.

***detection capability* (1.4.7):** The capability of a *measurement process* to distinguish small amounts of *analyte* from zero. It may be expressed in terms of the *minimum detectable concentration*.

***detection limit* (2.5, Table 2.1):** The smallest value of the amount or concentration of *analyte* that ensures a specified high probability of detection. Also called "*minimum detectable value.*"

***deviation reports* (9.2.2.2):** Documentation of any changes from the analysis plan that may affect data utility.

***digestion* (6.6):** (1) Heating a precipitate over time; used to form larger crystals after initial precipitation. (2) The dissolution of a *sample* by chemical means, typically through the addition of a strong acid or base.

***directed planning process* (1.2):** A systematic framework focused on defining the data needed to support an informed decision for a specific project. Directed planning provides a logic for setting well-defined, achievable objectives and developing a cost-effective, technically sound sampling and analysis design that balances the data user's tolerance for uncertainty in the decision process and the available resources for obtaining data to support a decision. Directed planning helps to eliminate poor or inadequate sampling and analysis designs.

***disproportionation (autoxidation-reduction)* (14.2.3):** An oxidation-reduction reaction in which a chemical species is simultaneously oxidized and reduced.

***dissolve* (6.5.1.1):** To form a solution by mixing a *solute* with a *solvent*. The particles of the *solute solvent* mix intimately at the atomic, molecular, and ionic levels with the particles of the *solvent*, and the *solute* particles are surrounded by particles of the *solvent*.

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***distillation* (12.2.1.2):** Separation of a volatile component(s) of a liquid mixture or solution by boiling the mixture to vaporize the component and subsequent condensation and collection of the components as a liquid.

***distribution* (3B.2):** The *distribution* of a *random variable* is a mathematical description of its possible values and their probabilities. The *distribution* is uniquely determined by its *distribution function*.

***distribution (partition) coefficient* (15.4.5.5):** An equilibrium constant that represents the ratio of the concentration of a *solute* distributed between two immiscible *solvents*.

***distribution function* (19A.1):** The *distribution function*, or *cumulative distribution function*, of a *random variable X* is the function F defined by $F(x) = \Pr[X \leq x]$.

***dose-based regulation* (2.3.2):** A regulation whose allowable *radionuclide* concentration limits are based on the dose received by an individual or population.

***dose equivalent* (2.5.2.1):** A quantity that expresses all radiations on a common scale for calculating the effective absorbed dose. This quantity is the product of absorbed dose (grays or rads) multiplied by a quality factor and any other modifying factors (MARSSIM, 2000). The "quality factor" adjusts the absorbed dose because not all types of ionizing radiation create the same effect on human tissue. For example, a *dose equivalent* of one sievert (Sv) requires 1 gray (Gy) of beta or gamma radiation, but only 0.05 Gy of alpha radiation or 0.1 Gy of neutron radiation. Because the sievert is a large unit, radiation doses often are expressed in millisieverts (mSv). See *committed effective dose equivalent* and *total effective dose equivalent*.

***duplicates* (1.4.8):** Two equal-sized samples of the material being analyzed, prepared, and analyzed separately as part of the same batch, used in the laboratory to measure the overall *precision* of the sample measurement process beginning with laboratory subsampling of the field *sample*.

***dynamic work plan* (4.4.2):** A type of work plan that specifies the decisionmaking logic to be used in the field to determine where the samples will be collected, when the sampling will stop, and what analyses will be performed. This is in contrast to a work plan that specifies the number of samples to be collected and the location of each *sample*.

***effective degrees of freedom* (ν_{eff}) (6A.2):** A parameter associated with a combined *standard uncertainty*, $u_c(y)$, analogous to the number of degrees of freedom for a Type A evaluation of *standard uncertainty*, which describes the reliability of the uncertainty estimate and which may

be used to select the coverage factor for a desired coverage probability. The number of effective degrees of freedom is determined using the *Welch-Satterthwaite formula*.

***efficiency* (2.5.4.2):** See *counting efficiency*.

***electrodeposition* (14.1):** Depositing (plating or coating) a metal onto the surface of an electrode by electrochemical reduction of its cations in solution.

***electronegativity* (14.2.2):** The ability of an atom to attract electrons in a covalent bond.

***electron density* (13.2.3):** A term representing the relative electron concentration in part of a molecule. The term indicates the unequal distribution of valence electrons in a molecule. Unequal distribution is the result of *electronegativity* differences of atoms in the bonds of the molecule and the geometry of the bonds; the results is a polar molecule.

***eluant* (14.7.4.1):** A liquid or solution acting as the moving phase in a chromatographic system.

***eluate* (14.7.4.1):** The liquid or solution that has passed over or through the *stationary phase* in a chromatographic system. The *eluate* may contain components of the analyzed solution, analytes, or impurities. In column chromatography, it is the liquid coming out of the column. The process is referred to as "eluting."

***emission probability per decay event* (E_e) (16.2.2):** The fraction of total decay events for which a particular particle or photon is emitted. Also called the "branching fraction" or "branching ratio."

***emulsion* (14.4.3):** (1) A *colloidal solution* in which both the dispersed phase and continuous phase are immiscible liquids (2) A permanent *colloidal solution* in which either the dispersed phase or continuous phase is water, usually oil in water or water in oil. See *gel*.

***environmental compliance* (4.2):** Agreement with environmental laws and regulations.

***environmental data collection process* (2.1):** Consists of a series of elements (e.g., planning, developing *project plan documents*, contracting for services, sampling, analysis, data verification, data validation, and *data quality assessment*), which are directed at the use of the data in decisionmaking.

***error (of measurement)* (1.4.7):** The difference between a measured result and the value of the *measurand*. The error of a measurement is primarily a theoretical concept, since its value is never known. See also *random error, systematic error,* and *uncertainty (of measurement)*.

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***estimator* (18B.2):** A *random variable* whose value is used to estimate an unknown parameter, θ, is called an *estimator* for θ. Generally, an estimator is a function of experimental data.

***exception* (8.2.3):** A concept in *data verification* meaning a failure to meet a requirement.

***excluded particles* (14.7.6):** Chemical components in a *gel-filtration chromatographic* system that do not enter the solid-phase matrix during separation; these components spend less time in the system and are the first to be eluted in a single fraction during chromatography.

***exclusion chromatography* (14.7.6):** See *gel-filtration chromatography*.

***excursion* (1.6.2):** Departure from the expected condition during laboratory analysis.

***expanded uncertainty* (1.4.7):** "The product, U, of the *combined standard uncertainty* of a measured value y and a *coverage factor k* chosen so that the interval from $y - U$ to $y + U$ has a desired high probability of containing the value of the *measurand*" (ISO, 1995).

***expectation* (19.2.2):** The *expectation* of a *random variable X*, denoted by $E(X)$ or μ_X, is a measure of the center of its *distribution* (a measure of central tendency) and is defined as a probability-weighted average of the possible numerical values. Other terms for the expectation value of X are the *expected value* and the *mean*.

***expected value* (18.3.2):** See *expectation*.

***expedited site characterization* (2.3.2):** A process used to identify all relevant contaminant migration pathways and determine the distribution, concentration, and fate of the contaminants for the purpose of evaluating risk, determining regulatory compliance, and designing remediation systems.

***experimental standard deviation* (6A.2):** A measure of the dispersion of the results of repeated measurements of the same quantity, given explicitly by

$$s(q_k) = \sqrt{\frac{1}{n-1}\sum_{k=1}^{n}(q_k - \bar{q})^2}$$

where $q_1, q_2, \ldots, q_n$ are the results of the measurements, and $\bar{q}$ is their arithmetic mean (ISO, 1993a).

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***external assessment* (4.2):** Part of the evaluation process used to measure the performance or effectiveness of a system and its elements. As an example, this could be information (audit, performance evaluation, inspection, etc.) related to a method's development, validation, and control that is done by personnel outside of the laboratory and is part of the laboratory *quality assurance* program.

***extraction chromatography* (14.4.4):** A solid-phase extraction method performed in a chromatographic column that uses a *resin* material consisting of an extractant absorbed onto an inert polymeric support matrix.

***false acceptance* (20.2.2):** See *Type II decision error*.

***false negative* (20.2.1):** See *Type II decision error*. MARLAP avoids the terms "*false negative*" and "*false positive*" because they may be confusing in some contexts.

***false positive* (14.10.9.9):** See *Type I decision error*. MARLAP avoids the terms "*false negative*" and "*false positive*" because they may be confusing in some contexts.

***false rejection* (20.2.1):** See *Type I decision error*.

***femtogram* (*fg*) (6.5.5.5):** Unit of mass equal to 10^{-15} grams.

***flocculation* (14.8.5):** See *coagulation* and *deflocculation*.

***formation constant* (14.3.2):** The equilibrium constant for the formation of a *complex ion* or coordination molecule. The magnitude of the constant represents the stability of the *complex*. Also called "stability constant."

***fractional distillation* (14.5.2):** Separation of liquid components of a mixture by repeated *volatilization* of the liquid components and condensation of their vapors within a *fractionation column*. Repeated *volatilization* and condensation produces a decreasing temperature gradient up the column that promotes the collection of the more volatile components (lower boiling point components) at the upper end of the column and return of the less volatile components at the lower end of the column. The process initially enriches the vapors in the more volatile components, and they separate first as lower boiling point fractions.

***fractionation column* (14.5.3):** A *distillation* column that allows repeated *volatilization* and condensation steps within the length of the column, accomplishing *fractional distillation* of components of a mixture in one *distillation* process by producing a temperature gradient that

decreases up the length of the column (see *fractional distillation*). The column is designed with plates or packing material inside the column to increase the surface area for condensation.

***frequency plots* (9.6.3):** Statisticians employ *frequency plots* to display the *imprecision* of a sampling and analytical event and to identify the type of distribution.

***fusion* (1.4.10):** See *sample dissolution*.

***full width of a peak at half maximum* (*FWHM*) (8.5.11):** A measure of the resolution of a spectral peak used in alpha or gamma spectrometry: the full peak-width energy (FW) at one-half maximum peak height (HM).

***full width of a peak at tenth maximum* (*FWTM*) (15.1):** A measure of the resolution of a spectral peak used in alpha or gamma spectrometry: the full peak-width energy (FW) at one-tenth maximum peak height (TM).

***gas chromatography* (*GC*) (14.5.2):** See *gas-liquid phase chromatography*.

***gas-liquid phase chromatography* (*GLPC*) (14.7.1):** A chromatographic separation process using a mobile gas phase (*carrier gas*) in conjunction with a low-volatility liquid phase that is absorbed onto an inert, solid-phase matrix to produce a *stationary phase*. The components of the analytical mixture are vaporized and swept through the column by the *carrier gas*.

***gel* (14.7.4.2, Table 14.9):** (1) A *colloidal solution* that is highly viscous, usually coagulated into a semirigid or jellylike solid. (2) Gelatinous masses formed from the *flocculation* of *emulsions*.

***gel-exclusion chromatography* (14.7.6):** See *gel-filtration chromatography*.

***gel-filtration chromatography* (14.7.6):** A column chromatographic separation process using a solid, inert polymeric matrix with pores that admit molecules less than a certain hydrodynamic size (molecular weight) but exclude larger molecules. The excluded molecules are separated from the included molecules by traveling only outside the matrix and are first eluted in bulk from the column. The included molecules, depending on size, spend different amounts of time in the pores of matrix and are separated by size.

***general analytical planning issues* (3.3):** Activities to be identified and resolved during a *directed planning process*. Typically, the resolution of *general analytical planning issues* normally results, at a minimum, in an *analyte* list, identified matrices of concern, *measurement*

quality objectives, and established frequencies and acceptance criteria for *quality control samples*.

***graded approach* (2.3):** A process of basing the level of management controls applied to an item or work on the intended use of the results and the degree of confidence needed in the quality of the results. MARLAP recommends a *graded approach* to project planning because of the diversity of environmental data collection activities. This diversity in the type of project and the data to be collected impacts the content and extent of the detail to be presented in the *project plan documents*.

***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*.

***GUM* (1.4.7):** *Guide to the Expression of Uncertainty in Measurement* (ISO, 1995).

***half-life* ($T_{½}$ *or* $t_{½}$) (1.4.8):** The time required for one-half of the atoms of a particular *radionuclide* in a *sample* to disintegrate or undergo nuclear transformation.

***heterogeneity* (2.5):** (1) "Spatial heterogeneity," a type of distributional heterogeneity, refers to the nonuniformity of the distribution of an *analyte* of concern within a matrix. Spatial heterogeneity affects sampling, sample processing, and sample preparation. See *homogenization*. (2) The "distributional heterogeneity" of a lot depends not only on the variations among particles but also on their spatial distribution. Thus, the distributional heterogeneity may change, for example, when the material is shaken or mixed. (3) The "constitutional" (or "compositional") heterogeneity of a lot is determined by variations among the particles without regard to their locations in the lot. It is an intrinsic property of the lot itself, which cannot be changed without altering individual particles.

***high-level waste* (*HLW*) (1.3):** (1) irradiated reactor fuel; (2) liquid wastes resulting from the operation of the first-cycle *solvent* extraction system, or equivalent, and the concentrated wastes from subsequent extraction cycles, or equivalent, in a facility for reprocessing irradiated reactor fuel; (3) solids into which such liquid wastes have been converted.

***high-pressure liquid chromatography* (*HPLC*) (14.7.7):** A column chromatography process using various solid-liquid phase systems in which the liquid phase is pumped through the system at high pressures. The process permits rapid, highly efficient separation when compared to many

other chromatographic systems and is, therefore, also referred to as "high-performance liquid chromatography."

***holdback carrier* (14.8.4.4):** A nonradioactive *carrier* of a *radionuclide* used to prevent that particular radioactive species from contaminating other radioactive species in a chemical operation (IUPAC, 2001).

***homogeneous distribution coefficient* (*D*) (14.8.4.1):** The equality constant in the equation representing the *homogeneous distribution law*. Values of *D* greater than one represent removal of a foreign *ion* by inclusion during *coprecipitation* (see *homogeneous distribution law*).

***homogeneous distribution law* (14.8.4.1):** A description of one mechanism in which *coprecipitation* by inclusion occurs (the less common mechanism). The amount of *ion* coprecipitating is linearly proportional to the ratio of the concentration of the *ion* in solution to the concentration of the coprecipitating agent in solution. Equilibrium between the precipitate and the solution is obtained (during digestion) and the crystals become completely homogeneous with respect to the foreign *ions* (impurities) (see *homogeneous distribution coefficient* and *digestion*).

***homogenization* (3.4, Table 3.1):** Producing a uniform distribution of analytes and particles throughout a *sample*.

***hydration* (14.3.1):** Association of water molecules with *ions* or molecules in solution.

***hydration sphere* (14.3.1):** Water molecules that are associated with *ions* or molecules in solution. The inner-hydration sphere (primary hydration sphere) consists of several water molecules directly bonded to *ions* through ion-dipole interactions and to molecules through dipole-dipole interactions including hydrogen bonding. The outer hydration sphere (secondary hydration sphere) is water molecules less tightly bound through hydrogen bonding to the molecules of the inner-hydration sphere.

***hydrolysis*:** (1) A chemical reaction of water with another compound in which either the compound or water is divided. (2) A reaction of water with *ions* that divides (lyses) water molecules to produce an excess of hydrogen *ions* or excess of hydroxyl *ions* in solution (an acidic or basic solution). Cations form *complex ions* with hydroxyl *ions* as *ligands* producing an acidic solution: $Fe^{+3} + H_2O \rightarrow Fe(OH)^{+2} + H^{+1}$. Anions form covalent bonds with the hydrogen *ion* producing weak acids and a basic solution: $F^{-1} + H_2O \rightarrow HF + OH^{-1}$.

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***hypothesis testing* (2.5, Table 2.1):** The use of statistical procedures to decide whether a *null hypothesis* should be rejected in favor of an *alternative hypothesis* or not rejected (see also *statistical test*).

***immobile phase* (14.7.1):** See *stationary phase*.

***imprecision* (1.4.8):** Variation of the results in a set of *replicate* measurements. This can be expressed as the *standard deviation* or coefficient of variation (*relative standard deviation*) (IUPAC, 1997). See *precision*.

***included particle* (14.7.6):** The chemical forms that are separated by *gel-filtration chromatography*. They enter the solid-phase matrix of the chromatographic system and are separated by hydrodynamic size (molecular weight), eluting in inverse order by size.

***inclusion* (14.7.1):** Replacement of an *ion* in a crystal lattice by a foreign *ion* similar in size and charge to form a mixed crystal or solid solution. Inclusion is one mechanism by which *ions* are *coprecipitated* with another substance precipitating from solution.

***in control* (1.6.2):** The analytical process has met the *quality control* acceptance criteria and project requirements. If the analytical process is *in control*, the assumption is that the analysis was performed within established limits and indicates a reasonable match among matrix, *analyte*, and *method*.

***independent* (19.2.2):** A collection of *random variables* $X_1, X_2, \ldots, X_n$ is *independent* if $\Pr[X_1 \le x_1, X_2 \le x_2, \ldots, X_n \le x_n] = \Pr[X_1 \le x_1] \cdot \Pr[X_2 \le x_2] \cdots \Pr[X_n \le x_n]$ for all real numbers $x_1, x_2, \ldots, x_n$. Intuitively, the collection is said to be *independent* if knowledge of the values of any subset of the variables provides no information about the likely values of the other variables.

***inferential statistics* (9.6.4.1):** Using data obtained from samples to make estimates about a population (inferential estimations) and to make decisions (*hypothesis testing*). Sampling and *inferential statistics* have identical goals: to use samples to make inferences about a population of interest and to use *sample* data to make defensible decisions.

***inner (primary) hydration sphere* (14.3.1):** See *hydration sphere*.

***input estimate* (3A.5):** Measured value of an input quantity. See *output estimate*.

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***input quantity* (6.5.5.1):** Any of the quantities in a mathematical measurement model whose values are measured and used to calculate the value of another quantity, called the *output quantity*. See *input estimate*.

***interferences* (1.4.9):** The presence of other chemicals or *radionuclides* in a *sample* that hinder the ability to analyze for the *radionuclide of interest*. See *method specificity*.

***ion-exchange chromatography* (6.6.2.3):** A separation method based on the reversible exchange of *ions* in a mobile phase with *ions* bonded to a solid ionic phase. *Ions* that are bonded less strongly to the solid phase (of opposite charge) are displaced by *ions* that are more strongly bonded. Separation of *analyte ions* depends on the relative strength of bonding to the solid phase. Those less strongly bonded *ions* are released from the solid phase earlier and eluted sooner.

***ion-product* (14.8.3.1):** The number calculated by substituting the molar concentration of *ions* that could form a precipitate into the solubility-product expression of the precipitating compound. The *ion-product* is used to determine if a precipitate will form from the concentration of *ions* in solution. If the *ion-product* is larger than the *solubility-product constant*, precipitation will occur; if it is smaller, precipitation will not occur.

***isomeric transition* (14.10.9.12):** The transition, via gamma-ray emission (or internal conversion), of a nucleus from a high-energy state to a lower-energy state without accompanying particle emission, e.g., $^{99m}Tc \rightarrow {}^{99}Tc + \gamma$.

***isotope* (3.3.4):** Any of two or more nuclides having the same number of protons in their nuclei (same atomic number), but differing in the number of neutrons (different mass numbers, for example ^{58}Co, ^{59}Co, and ^{60}Co). See *radionuclide*.

***isotope dilution analysis* (14.10.7):** A method of quantitative analysis based on the measurement of the isotopic abundance of an element after isotopic dilution of the test portion.

***key analytical planning issue* (1.6.1):** An issue that has a significant effect on the selection and development of analytical protocols or an issue that has the potential to be a significant contributor of uncertainty to the analytical process and ultimately the resulting data.

***laboratory control sample* (2.5.4.2):** A standard material of known composition or an artificial *sample* (created by fortification of a clean material similar in nature to the sample), which is prepared and analyzed in the same manner as the sample. In an ideal situation, the result of an analysis of the *laboratory control sample* should be equivalent to (give 100 percent of) the *target*

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analyte concentration or *activity* known to be present in the fortified sample or standard material. The result normally is expressed as percent *recovery*. See also *quality control sample*.

***Laboratory Information Management System* (*LIMS*) (11.2.1):** An automated information system used at a laboratory to collect and track data regarding sample analysis, laboratory *quality control* operability information, final result calculation, report generation, etc.

***laboratory method* (6.2):** Includes all physical, chemical, and radiometric processes conducted at a laboratory in order to provide an analytical result. These processes may include sample preparation, dissolution, chemical separation, mounting for counting, nuclear instrumentation counting, and analytical calculations. Also called *analytical method*.

***law of propagation of uncertainty* (19.1):** See *uncertainty propagation formula*.

***level of confidence* (1.4.11):** See *coverage probability*.

***ligand* (14.3.1):** A molecule, atom, or *ion* that donates at least one electron pair to a metal atom or *ion* to form a coordination molecule or *complex ion*. See *dentate*.

***linearity* (7.2.2.5):** The degree to which the response curve for a measuring device, such as an analytical balance, follows a straight line between the calibration points. The *linearity* is usually specified by the maximum deviation of the response curve from such a straight line.

***liquid chromatography* (*LC*) (14.7.1):** A chromatographic process using a mobile liquid-phase.

***liquid-phase chromatography* (*LPC*) (14.7.1):** A chromatographic process in which the mobile and *stationary phases* are both liquids. Separation is based on relative solubility between two liquid phases. The *stationary phase* is a nonvolatile liquid coated onto an inert solid matrix or a liquid trapped in or bound to a solid matrix. Also called "liquid-partition chromatography."

***logarithmic distribution coefficient* (λ) (14.8.4.1):** The equality constant in the equation representing the *Logarithmic Distribution Law*. Values of λ greater than one represent removal of a foreign *ion* by inclusion during *coprecipitation*, and the larger the value, the more effective and selective the process is for a specific *ion*. Generally, the *logarithmic distribution coefficient* decreases with temperature, so *coprecipitation* by inclusion is favored by lower temperature.

***Logarithmic Distribution Law* (14.8.4.1):** A description of one mechanism by which *coprecipitation* by inclusion occurs (the more common mechanism). The amount of *ion* coprecipitated is logarithmically proportional to the amount of primary *ion* in the solution during

crystallization. Crystal are grown in a slow and orderly process, such as precipitation from homogeneous solution, and each crystal surface, as it is formed, is in equilibrium with the solution. As a result, the concentration of a foreign *ion* (impurity) varies continuously from the center to the periphery of the crystal (see *logarithmic distribution coefficient*).

***logic statement* (2.6):** The output from the *directed planning process* about what must be done to obtain the desired answer.

***lower limit of detection* (*LLD*) (14.10.9.5):** (1) "The smallest concentration of radioactive material in a *sample* that will yield a net count, above the measurement process (MP) blank, that will be detected with at least 95 percent probability with no greater than a 5 percent probability of falsely concluding that a blank observation represents a 'real' signal" (NRC, 1984). (2) "An estimated detection limit that is related to the characteristics of the counting instrument" (EPA, 1980).

***low-pressure chromatography* (14.7.1):** Column chromatography in which a liquid phase is passed through a column under pressure supplied by gravity or a low-pressure pump.

***Lucas cell* (10.5.4.4):** A specially designed, high-efficiency cell for the analysis of radon gas with its progeny. The cell is coated with a zinc sulfide phosphor material that releases ultraviolet light when the alpha particles from radon and its progeny interact with the phosphor.

***Marinelli beaker* (6.5.3):** A counting container that allows the *source* to surround the detector, thus maximizing the geometrical efficiency. It consists of a cylindrical sample container with an inverted well in the bottom that fits over the detector. Also called a "reentrant beaker."

***MARLAP Process* (1.4):** A performance-based approach that develops *Analytical Protocol Specifications*, and uses these requirements as criteria for the analytical protocol selection, development, and evaluation processes, and as criteria for the evaluation of the resulting laboratory data. This process, which spans the three phases of the *data life cycle* for a project, is the basis for achieving MARLAP's basic goal of ensuring that radioanalytical data will meet a project's or program's data requirements or needs.

***masking* (14.4.3):** The prevention of reactions that are normally expected to occur through the presence or addition of a masking agent (reagent).

***masking agent* (14.4.3):** A substance that is responsible for converting a chemical form, which would have otherwise participated in some usual chemical reaction, into a derivative that will not participate in the reaction.

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***matrix of concern* (1.4.10):** Those matrices identified during the directed project planning process from which samples may be taken. Typical matrices include: surface soil, subsurface soil, sediment, surface water, ground water, drinking water, process effluents or wastes, air particulates, biota, structural materials, and metals.

***matrix-specific analytical planning issue* (3.1):** Key analytical planning issue specific to that matrix, such as filtration and preservation issues for water samples.

***matrix spike* (3.3.10):** An *aliquant* of a *sample* prepared by adding a known quantity of *target analytes* to specified amount of matrix and subjected to the entire analytical procedure to establish if the method or procedure is appropriate for the analysis of the particular matrix.

***matrix spike duplicate* (*MSD*) (9.6.3):** A second *replicate* matrix spike prepared in the laboratory and analyzed to evaluate the *precision* of the measurement process.

***Maximum Contaminant Level* (*MCL*) (2.5.2.1):** The highest level of a contaminant that is allowed in drinking water. MCLs are set as close as feasible to the level believed to cause no human health impact, while using the best available treatment technology and taking cost into consideration. MCLs are enforceable standards.

***mean* (1.4.8):** See *expectation* (compare with *arithmetic mean* and *sample mean*).

***mean concentration* (2.5.2.3):** A weighted average of all the possible values of an *analyte* concentration, where the weight of a value is determined by its probability.

***measurand* (1.4.7):** "Particular quantity subject to measurement"(ISO, 1993a).

***measurement performance criteria* (1.2):** See *measurement quality objectives*.

***measurement process* (1.3):** *Analytical method* of defined structure that has been brought into a state of statistical control, such that its imprecision and bias are fixed, given the measurement conditions (IUPAC, 1995).

***measurement quality objective* (*MQO*) (1.4.9):** The analytical data requirements of the *data quality objectives* are project- or program-specific and can be quantitative or qualitative. These analytical data requirements serve as *measurement performance criteria* or objectives of the analytical process. MARLAP refers to these performance objectives as *measurement quality objectives (MQOs)*. Examples of quantitative *MQOs* include statements of required *analyte* detectability and the uncertainty of the analytical protocol at a specified *radionuclide* concentra-

tion, such as the *action level*. Examples of qualitative *MQOs* include statements of the required specificity of the analytical protocol, e.g., the ability to analyze for the *radionuclide of interest* given the presence of interferences.

***measurement uncertainty* (1.4.7):** See *uncertainty (of measurement)*.

***measurement variability* (2.5.2.2):** The variability in the measurement data for a *survey unit* is a combination of the *imprecision* of the measurement process and the real spatial variability of the *analyte* concentration.

***median* (9.6.4.1):** A *median* of a distribution is any number that splits the range of possible values into two equally likely portions, or, to be more rigorous, a 0.5-*quantile*. See *arithmetic mean*.

***method* (1.4.5):** See *analytical method*.

***method blank* (Figure 3.3):** A *sample* assumed to be essentially *target analyte*-free that is carried through the radiochemical preparation, analysis, mounting and measurement process in the same manner as a routine sample of a given matrix.

***method control* (6.1):** Those functions and steps taken to ensure that the validated method as routinely used produces data values within the limits of the *measurement quality objectives*. *Method control* is synonymous with process control in most *quality assurance* programs.

***method detection limit* (*MDL*) (3B.4):** "The minimum concentration of a substance that can be measured and reported with 99 percent confidence that the *analyte* concentration is greater than zero … determined from analysis of a *sample* in a given matrix containing the *analyte*" (40 CFR 136, Appendix B).

***method performance characteristics* (3.3.7):** The characteristics of a specific *analytical method* such as *method uncertainty*, *method range*, *method specificity*, and *method ruggedness*. MARLAP recommends developing *measurement quality objectives* for select *method performance characteristics*, particularly for the *uncertainty (of measurement)* at a specified concentration (typically the *action level*).

***method range* (1.4.9):** The lowest and highest concentration of an *analyte* that a method can accurately detect.

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***method ruggedness* (1.4.9):** The relative stability of method performance for small variations in method parameter values.

***method specificity* (1.4.9):** The ability of the method to measure the *analyte* of concern in the presence of interferences.

***method uncertainty* (3.3.7):** Method uncertainty refers 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. Although individual measurement uncertainties will vary from one measured result to another, the required *method uncertainty* is a target value for the individual measurement uncertainties, and is an estimate of *uncertainty (of measurement)* before the sample is actually measured. See also *uncertainty (of measurement)*.

***method validation* (5.3):** The demonstration 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*. See *project method validation*.

***method validation reference material* (*MVRM*) (5.5.2):** Reference materials that have the same or similar chemical and physical properties as the proposed project samples, which can be used to validate the laboratory's methods.

***metrology* (1.4.7):** The science of measurement.

***minimum detectable amount* (*MDA*) (3B.3):** The minimum detectable value of the amount of analyte in a sample. Same definition as the *minimum detectable concentration* but related to the quantity (activity) of a *radionuclide* rather than the concentration of a *radionuclide*. May be called the "minimum detectable activity" when used to mean the *activity* of a radionuclide (see ANSI N13.30 and N42.23).

***minimum detectable concentration* (*MDC*) (2.5.3):** The *minimum detectable value* of the analyte concentration in a sample. ISO refers to the MDC as the *minimum detectable value of the net state variable*. They define this as the smallest (true) value of the net state variable that gives a specified probability that the value of the response variable will exceed its critical value—i.e., that the material analyzed is not blank.

***minimum detectable value* (20.2.1):** An estimate of the smallest true value of the *measurand* that ensures a specified high probability, $1 - \beta$, of detection. The definition of the *minimum*

detectable value presupposes that an appropriate detection criterion has been specified (see *critical value*).

***minimum quantifiable concentration* (*MQC*) (3.3.7):** The *minimum quantifiable concentration*, or the *minimum quantifiable value* of the *analyte* concentration, is defined as the smallest concentration of *analyte* whose presence in a laboratory *sample* ensures the relative *standard deviation* of the measurement does not exceed a specified value, usually 10 percent.

***minimum quantifiable value* (20.2.7):** The smallest value of the *measurand* that ensures the *relative standard deviation* of the measurement does not exceed a specified value, usually 10 percent (see also *minimum quantifiable concentration*).

***mixed waste* (1.3):** Waste that contains both radioactive and hazardous chemicals.

***mobile phase* (14.7.1):** The phase in a chromatographic system that is moving with respect to the *stationary phase*; either a liquid or a gas phase.

***moving phase* (14.7.1):** See *mobile phase*.

***net count rate*: (16.3.2):** The *net count rate* is the value resulting form the subtraction of the background count rate (instrument background or appropriate blank) from the total (gross) count rate of a *source* or sample.

***nonaqueous samples* (10.3.5):** Liquid-sample matrices consisting of a wide range of organic/ *solvents,* organic compounds dissolved in water, oils, lubricants, etc.

***nonconformance* (5.3.7):** An instance in which the contractor does not meet the performance criteria of the contract or departs from contract requirements or acceptable practice.

***nuclear decay* (15.3):** A spontaneous nuclear transformation.

***nuclear counting* (1.6):** The measurement of alpha, beta or photon emissions from *radionuclides*.

***nuclide* (1.1):** A species of atom, characterized by its mass number, atomic number, and nuclear energy state, providing that the mean *half-life* in that state is long enough to be observable (IUPAC, 1995).

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***nuclide-specific analysis* (3.3.8.3):** Radiochemical analysis performed to isolate and measure a specific *radionuclide*.

***null hypothesis* (H_0) (2.5, Table 2.1):** One of two mutually exclusive statements tested in a statistical *hypothesis test* (compare with *alternative hypothesis*). The *null hypothesis* is presumed to be true unless the test provides sufficient evidence to the contrary, in which case the *null hypothesis* is rejected and the *alternative hypothesis* is accepted.

***occlusion* (14.8.3.1):** The mechanical entrapment of a foreign *ion* between subsequent layers during crystal formation. A mechanism of *coprecipitation*.

***Ostwald ripening* (14.8.3.2):** Growth of larger crystals during precipitation by first dissolving smaller crystals and allowing the larger crystals to form.

***outer (secondary) hydration sphere* (14.3.1):** See *hydration sphere*.

***outlier* (9.6.4.1):** A value in a group of observations, so far separated from the remainder of the values as to suggest that they may be from a different population, or the result of an error in measurement (ISO, 1993b).

***output estimate* (3A.5):** The calculated value of an output quantity (see *input estimate*).

***output quantity* (19.3.2):** The quantity in a mathematical measurement model whose value is calculated from the measured values of other quantities in the model (see *input quantity* and *output estimate*).

***oxidation* (6.4):** The increase in oxidation number of an atom in a chemical form during a chemical reaction. Increase in oxidation number is a result of the loss of electron(s) by the atom or the decrease in electron density when the atom bonds to a more electronegative element or breaks a bond to a less electronegative element.

***oxidation-reduction (redox) reaction* (10.3.3):** A chemical reaction in which electrons are redistributed among the atoms, molecules, or *ions* in the reaction.

***oxidation number* (6.4):** An arbitrary number indicating the relative electron density of an atom or *ion* of an element in the combined state, relative to the electron density of the element in the pure state. The oxidation number increases as the electron density decreases and decreases as the electron density increases.

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***oxidation state* (6.4):** See *oxidation number*.

***oxidizing agent* (10.5.2):** The chemical species in an oxidation-reduction reaction that causes oxidation of another chemical species by accepting or attracting electrons. The oxidizing agent is reduced during the reaction.

***paper chromatography* (14.7.1):** A chromatographic process in which the *stationary phase* is some type of absorbent paper. The *mobile phase* is a pure liquid or solution.

***parameter of interest* (2.5, Table 2.1):** A descriptive measure (e.g., *mean*, median, or proportion) that specifies the characteristic or attribute that the decisionmaker would like to know and that the data will estimate.

***PARCC* (3.3.7):** "Precision, accuracy, representativeness, comparability, and completeness." See *data quality indicators*.

***parent radionuclide* (3.3.4):** The initial *radionuclide* in a *decay chain* that decays to form one or more *progeny*.

***partition (distribution) coefficient*:** See *distribution coefficient*.

***peptization*:** See *deflocculation*.

***percentile* (19A.1):** If X is a random variable and p is a number between 0 and 1, then a $100p^{th}$ percentile of X is any number x_p such that the probability that $X < x_p$ is at most p and the probability that $X \le x_p$ is at least p. For example, if $x_{0.95}$ is a 95th percentile of X then $\Pr[X < x_{0.95}] \le 0.95$ and $\Pr[X \le x_{0.95}] \ge 0.95$. See *quantile*.

***performance-based approach* (1.2):** Defining the analytical data needs and requirements of a project in terms of measurable goals during the planning phase of a project. In a *performance-based approach*, the project-specific analytical data requirements that are determined during a *directed planning process* serve as measurement performance criteria for selections and decisions on how the laboratory analyses will be conducted. The project-specific analytical data requirements are also used for the initial, ongoing, and final evaluation of the laboratory's performance and the laboratory data.

***performance-based approach to method selection* (6.1):** The process wherein a validated method is selected based on a demonstrated capability to meet defined quality and laboratory performance criteria.

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***performance evaluation program* (5.3.5):** A laboratory's participation in an internal or external program of analyzing performance testing samples appropriate for the analytes and matrices under consideration (i.e., *performance evaluation (PE) program* traceable to a national standards body, such as the National Institute of Standards and Technology in the United States).

***performance evaluation sample* (3.3.10):** Reference material samples used to evaluate the performance of the laboratory. Also called *performance testing (PT)* samples or materials.

***performance indicator* (1.6.2):** Instrument- or protocol-related parameter routinely monitored to assess the laboratory's estimate of such controls as chemical yield, instrument background, *uncertainty (of measurement)*, *precision*, and *bias*.

***performance testing (PT)*:** See *performance evaluation program*.

***picocurie* (*pCi*) (1.4.9):** 10^{-12} *curie*.

***planchet* (10.3.2):** A metallic disk (with or without a raised edge) that is used for the analysis of a radioactive material after the material has been filtered, evaporated, electroplated, or dried. Evaporation of water samples for gross alpha and beta analysis often will take place directly in the planchet.

***Poisson distribution* (18.3.2):** A random variable X has the *Poisson distribution* with parameter λ if for any nonnegative integer k,

$$\Pr[X = k] = \frac{\lambda^k e^{-\lambda}}{k!}$$

In this case both the *mean* and *variance* of X are numerically equal to λ. The *Poisson distribution* is often used as a model for the result of a nuclear counting measurement.

***polymorphism* (14.8.3.1):** The existence of a chemical substance in two or more physical forms, such as different crystalline forms.

***postprecipitation* (14.8.4.3):** The subsequent precipitation of a chemically different species upon the surface of an initial precipitate; usually, but not necessarily, including a common *ion* (IUPAC, 1997).

***precision* (1.4.8):** The closeness of agreement between independent test results obtained by applying the experimental procedure under stipulated conditions. *Precision* may be expressed as the *standard deviation* (IUPAC, 1997). See *imprecision*.

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***prescribed methods* (6.1):** Methods that have been selected by the industry for internal use or by a regulatory agency for specific programs. Methods that have been validated for a specific application by national standard setting organizations, such as ASTM, ANSI, AOAC, etc., may also be used as prescribed methods by industry and government agencies.

***primary (inner) hydration sphere* (14.3.1):** See *hydration sphere*.

***primordial radionuclide* (3.3.1):** A naturally occurring *radionuclide* found in the earth that has existed since the formation (~4.5 billion years) of the Earth, e.g., ^{232}Th and ^{238}U.

***principal decision* (2.7.3):** The *principal decision* or study question for a project is identified during Step 2 of the *data quality objectives* process. The *principal decision* could be simple, like whether a particular discharge is or is not in compliance, or it could be complex, such as determining if an observed adverse health effect is being caused by a nonpoint source discharge.

***principal study question* (2.7.3):** See *principal decision*.

***probabilistic sampling plan* (9.6.2.3):** Using assumptions regarding average concentrations and variances of samples and matrix by the planning team during the development of the sampling plan.

***probability* (1.4.7):** "A real number in the scale 0 to 1 attached to a random event" (ISO, 1993b). The probability of an event may be interpreted in more than one way. When the event in question is a particular outcome of an experiment (or measurement), the probability of the event may describe the relative frequency of the event in many trials of the experiment, or it may describe one's degree of belief that the event occurs (or will occur) in a single trial.

***probability density function* (*pdf*) (19A.1):** A *probability density function* for a *random variable* X is a function $f(x)$ such that the probability of any event $a \le X \le b$ is equal to the value of the integral $\int_a^b f(x)\,dx$. The *pdf*, when it exists, equals the derivative of the distribution function.

***process knowledge* (1.4.10):** Information about the *radionuclide*(s) of concern derived from historical knowledge about the production of the sampled matrix or waste stream.

***progeny* (3.3.4):** The product resulting from the radioactive disintegration or nuclear transformation of its parent *radionuclide*. See *decay chain*.

***project method validation* (6.1):** The demonstrated method applicability for a particular project. See *method validation*.

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project narrative statement **(4.3):** Description of environmental data collection activities, such as basic studies or small projects, which only require a discussion of the experimental process and its objectives. Other titles used for project narrative statements are *quality assurance* narrative statement and proposal *quality assurance* plan. Basic studies and small projects generally are of short duration or of limited scope and could include proof of concept studies, exploratory projects, small data collection tasks, feasibility studies, qualitative screens, or initial work to explore assumptions or correlations.

project plan documents **(1.1):** Gives the data user's expectations and requirements, which are developed during the planning process, where the *Analytical Protocol Specifications* (which include the *measurement quality objectives*) are documented, along with the *standard operating procedures*, health and safety protocols and *quality assurance/quality control* procedures for the field and laboratory analytical teams. Project plan, work plan, *quality assurance project plan*, field sampling plan, *sampling and analysis plan*, and *dynamic work plan* are some of the names commonly used for *project plan documents*.

project planning team **(2.1):** Consists of all the parties who have a vested interest or can influence the outcome (*stakeholders*), such as program and project managers, regulators, the public, project engineers, health and safety advisors, and specialists in statistics, health physics, chemical analysis, radiochemical analysis, field sampling, *quality assurance*, *quality control*, data assessment, hydrology and geology, contract management, and field operation. The *project planning team* will define the decision(s) to be made (or the question the project will attempt to resolve) and the inputs and boundaries to the decision using a *directed planning process*.

project quality objectives **(2.1):** See *decision performance criteria* and *data quality objective*.

project specific plan **(4.3):** Addresses design, work processes, and inspection, and incorporates, by citation, site-wide plans that address records management, quality improvement, procurement, and assessment.

propagation of uncertainty **(15.2.5):** See *uncertainty propagation*.

protocol **(1.4.3):** See *analytical protocol*.

protocol performance demonstration **(3.1):** See *method validation*.

qualifiers **(8.1):** Code applied to the data by a data validator to indicate a verifiable or potential data deficiency or *bias* (EPA, 2002).

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***quality assurance* (*QA*) (1.3):** An integrated system of management activities involving planning, implementation, assessment, reporting, and quality improvement to ensure that a process, item, or service is of the type and quality needed and expected.

***quality assurance project plan* (*QAPP*) (1.4.11):** A formal document describing in detail the necessary *quality assurance*, *quality control*, and other technical activities that must be implemented to ensure that the results of the work performed will satisfy the stated performance criteria. The QAPP describes policy, organization, and functional activities and the *data quality objectives* and measures necessary to achieve adequate data for use in selecting the appropriate remedy.

***quality control* (*QC*) (1.4.3):** The overall system of technical activities whose purpose is to measure and control the quality of a process or service so that it meets the needs of the users or performance objectives.

***quality control sample* (1.4.3):** Sample analyzed for the purpose of assessing *imprecision* and *bias*. See also *blanks*, *matrix spikes*, *replicates*, and *laboratory control sample*.

***quality control test* (8.5.1):** Comparison of *quality control* results with stipulated acceptance criteria.

***quality indicator* (2.5.4.2):** Measurable attribute of the attainment of the necessary quality for a particular environmental decision. *Precision*, *bias*, *completeness*, and *sensitivity* are common *data quality indicators* for which quantitative *measurement quality objectives* could be developed during the planning process.

***quality system* (9.2.2.3):** The *quality system* oversees the implementation of *quality control samples*, documentation of *quality control sample* compliance or noncompliance with *measurement quality objectives*, audits, surveillances, performance evaluation sample analyses, corrective actions, quality improvement, and reports to management.

***quantification capability* (1.4.9):** The ability of a measurement process to quantify the *measurand* precisely, usually expressed in terms of the *minimum quantifiable value*.

***quantification limit* (20.2.1):** See *minimum quantifiable value*.

***quantile* (6.6.2, Table 6.1):** A *p-quantile* of a *random variable X* is any value x_p such that the probability that $X < x_p$ is at most p and the probability that $X \leq x_p$ is at least p. (See *percentile*.)

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***quench* (7.2):** A term used to describe the process in liquid-scintillation counting when the production of light is inhibited or the light signal is partially absorbed during the transfer of light to the photocathode.

***radioactive* (1.1):** Exhibiting *radioactivity*, or containing *radionuclides*.

***radioactive decay* (3A.4):** "Nuclear decay in which particles or electromagnetic radiation are emitted or the nucleus undergoes spontaneous fission or electron capture." (IUPAC, 1994)

***radioactive equilibrium* (3.3.4):** One of three distinct relationships that arise when a radionuclide decays and creates progeny that are also radioactive: (1) secular equilibrium occurs when *half-life* of the progeny is much less than the *half-life* of the parent (for a single progeny, the total activity reaches a maximum of about twice the initial activity, and then displays the characteristic *half-life* of the parent—usually no change over normal measurement intervals); (2) transient equilibrium occurs when the *half-life* of the progeny is less than the *half-life* of the parent (for a single progeny, total activity passes through a maximum, and then decreases with the characteristic *half-life* of the parent); and (3) no equilibrium occurs when the *half-life* of the progeny is greater than the *half-life* of the parent (total activity decreases continually after time zero).

***radioactivity* (2.5.4.1):** The property of certain nuclides of undergoing *radioactive decay*.

***radioanalytical specialist* (2.1):** Key technical experts who participate on the *project planning team*. *Radioanalytical specialists* may provide expertise in radiochemistry and radiation/nuclide measurement systems, and have knowledge of the characteristics of the analytes of concern to evaluate their fate and transport. They may also provide knowledge about sample transportation issues, preparation, preservation, sample size, subsampling, available analytical protocols, and achievable analytical data quality.

***radiochemical analysis* (5.3.5):** The analysis of a sample matrix for its *radionuclide* content, both qualitatively and quantitatively.

***radiocolloid* (14.4.6.2):** A colloidal form of a *radionuclide* tracer produced by sorption of the *radionuclide* onto a preexisting colloidal impurity, such as dust, cellulose fibers, glass fragments, organic material, and polymeric metal hydrolysis products, or by polycondensation of a monomeric species consisting of aggregates of a thousand to ten million radioactive atoms.

***radiological holding time* (6.5):** The time required to process the *sample*. Also refers to the time differential between the sample collection date and the final sample counting (analysis) date.

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***radiolysis* (14.1):** Decomposition of any material as a result of exposure to radiation.

***radionuclide* (1.1):** A nuclide that is *radioactive* (capable of undergoing *radioactive decay*).

***radionuclide of interest* (1.4.10):** The *radionuclide* or *target analyte* that the planning team has determined important for a project. Also called *radionuclide of concern* or *target radionuclide*.

***radiotracer* (6.5.2):** (1) A radioactive isotope of the *analyte* that is added to the *sample* to measure any losses of the *analyte* during the *chemical separations* or other processes employed in the analysis (the chemical yield). (2) A radioactive element that is present in only extremely minute quantities, on the order of 10^{-15} to 10^{-11} Molar.

***random effect* (3A.4):** Any effect in a measurement process that causes the measured result to vary randomly when the measurement is repeated.

***random error* (3A.4):** A result of a measurement minus the mean that would result from an infinite number of measurements of the same *measurand* carried out under repeatability conditions (ISO, 1993a).

***random variable* (19.3.1):** The numerical outcome of an experiment, such as a laboratory measurement, that produces varying results when repeated.

***reagent blank* (12.6.5):** Consists of the analytical reagent(s) in the procedure without the *target analyte* or sample matrix, introduced into the analytical procedure at the appropriate point and carried through all subsequent steps to determine the contribution of the reagents and of the involved analytical steps.

***recovery* (2.5.4.2):** The ratio of the amount of *analyte* measured in a spiked or *laboratory control sample*, to the amount of *analyte* added, and is usually expressed as a percentage. For a matrix spike, the measured amount of *analyte* is first decreased by the measured amount of *analyte* in the sample that was present before spiking. Compare with *yield*.

***redox* (13.2.3):** An acronym for *oxidation-reduction*.

***reducing agent* (13.4.1, Table 13.2):** The chemical in an oxidation-reduction reaction that reduces another chemical by providing electrons. The *reducing agent* is oxidized during the reaction.

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***reducing; reduction* (13.4.1, Table 13.2):** The decrease in oxidation number of an atom in a chemical form during a chemical reaction. The decrease is a result of the gain of electron(s) by an atom or the increase in electron density by an atom when it bonds to a less electronegative element or breaks a bond to a more electronegative element.

***regulatory decision limit* (2.5.2.1):** The numerical value that will cause the decisionmaker to choose one of the alternative actions. An example of such a limit for drinking water is the *maximum contaminant level (MCL)*. See *action level*.

***rejected result* (8.3.3):** A result that is unusable for the intended purpose. A result should only be rejected when the risks of using it are significant relative to the benefits of using whatever information it carries. *Rejected data* should be qualified as such and not used in the *data quality assessment* phase of the *data life cycle*.

***relative standard deviation* (*RSD*) (6.5.5.2):** See *coefficient of variation*.

***relative standard uncertainty* (3.3.7.1.2):** The ratio of the *standard uncertainty* of a measured result to the result itself. The relative *standard uncertainty* of x may be denoted by $u_r(x)$.

***relative variance* (19A.1):** The *relative variance* of a *random variable* is the square of the coefficient of variation.

***release criterion* (1.3):** A regulatory limit expressed in terms of dose or risk. The release criterion is typically based on the *total effective dose equivalent (TEDE)*, the *committed effective dose equivalent (CEDE)*, risk of cancer incidence (morbidity), or risk of cancer death (mortality), and generally can not be measured directly.

***repeatability (of results of measurement)* (6.6):** The closeness of the agreement between the results of successive measurements of the same *measurand* carried out under the same "repeatability conditions" of measurement. "Repeatability conditions" include the same measurement procedure, the same observer (or analyst), the same measuring instrument used under the same conditions, the same location, and repetition over a short period of time. *Repeatability* may be expressed quantitatively in terms of the dispersion characteristics of the results (Adapted from ISO, 1993a.).

***replicates* (3.3.10):** Two or more *aliquants* of a homogeneous *sample* whose independent measurements are used to determine the *precision* of laboratory preparation and analytical procedures.

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***representativeness* (2.5.4):** (1) The degree to which samples properly reflect their parent populations. (2) A representative *sample* is a sample collected in such a manner that it reflects one or more characteristics of interest (as defined by the project objectives) of a population from which it was collected. (3) One of the five principal *data quality indicators* (*precision*, *bias*, *representativeness*, *comparability*, and *completeness*).

***reproducibility (of results of measurement)* (6.4):** The closeness of the agreement between the results of measurements of the same *measurand* carried out under changed conditions of measurement. A valid statement of *reproducibility* requires specification of the conditions changed. The changed conditions may include principle of measurement, method of measurement, observer (or analyst), measuring instrument, reference standard, location, conditions of use, and time. *Reproducibility* may be expressed quantitatively in terms of the dispersion characteristics of the results. Results are usually understood to be corrected results. (Adapted from ISO, 1993a.).

***request for proposals* (*RFP*) (5.1):** An advertisement from a contracting agency to solicit proposals from outside providers during a negotiated procurement. See *statement of work*.

***required minimum detectable concentration* (*RMDC*) (8.5.3.2):** An upper limit for the *minimum detectable concentration* required by some projects.

***resin* (14.4.5.1):** A synthetic or naturally occurring polymer used in *ion-exchange chromatography* as the solid *stationary phase*.

***resolution* (8.5.1.11):** The peak definition of alpha, gamma-ray, and liquid-scintillation spectrometers, in terms of the *full width of a peak at half maximum (FWHM)*, which can be used to assess the adequacy of instrument setup, detector *sensitivity*, and chemical separation techniques that may affect the identification, specification, and quantification of the *analyte*.

***response variable* (20.2.1):** The variable that gives the observable result of a measurement—in radiochemistry, typically a gross count or count rate.

***robustness* (5.3.9):** The ability of a method to deal with large fluctuations in interference levels and variations in matrix. (See *method ruggedness*.)

***ruggedness* (1.4.9):** See *method ruggedness*.

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***sample* (1.1):** (1) A portion of material selected from a larger quantity of material. (2) A set of individual samples or measurements drawn from a population whose properties are studied to gain information about the entire population.

***sample descriptors* (8.5.1.1):** Information that should be supplied to the laboratory including sample ID, *analytical method* to be used, *analyte*, and matrix.

***sample digestion* (1.4.6):** Solubilizing an *analyte* or analytes and its host matrix. Acid digestion, fusion, and microwave digestion are some common *sample digestion* techniques.

***sample dissolution* (1.1):** See *sample digestion*.

***sample management* (2.7.2):** Includes administrative and *quality assurance* aspects covering sample receipt, control, storage, and disposition.

***sample mean* (9.6.4.2):** An estimate of the mean of the *distribution* calculated form a statistical sample of observations. The *sample mean* equals the sum of the observed values divided by the number of values, *N*. If the observed values are $x_1, x_2, x_3, \ldots, x_N$, then the *sample mean* is given by

$$\text{sample mean} = \frac{\sum_{i=1}^{N} x_i}{N}$$

***sample population* (3.3.7.1.2):** A set of individual samples or measurements drawn from a population whose properties are studied to gain information about the entire population.

***sample processing turnaround time* (5.3.6):** The time differential from the receipt of the sample at the laboratory to the reporting of the analytical results.

***sample tracking* (1.4.5):** Identifying and following a *sample* through the steps of the analytical process including: field sample preparation and preservation; sample receipt and inspection; laboratory sample preparation; *sample dissolution*; chemical separation of *radionuclides of interest*; preparation of sample for instrument measurement; instrument measurement; and data reduction and reporting.

***sample variance* (9.6.4.2):** An estimate of the *variance* of a distribution calculated from a statistical sample of observations. If the observed values are $x_1, x_2, x_3, \ldots, x_N$, and the sample mean is $\bar{x}$, then the *sample variance* is given by:

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$$s^2 = \frac{1}{N-1}\sum_{i=1}^{N}(x_i - \bar{x})^2$$

***sampling and analysis plan* (*SAP*) (1.5):** See *project plan documents*.

***saturated solution* (14.8.2):** A solution that contains the maximum amount of substance that can dissolve in a prescribed amount of *solvent* at a given temperature. The dissolved substance is in equilibrium with any undissolved substance.

***scale of decision* (2.5, Table 2.1):** The spatial and temporal bounds to which the decision will apply. The *scale of decision* selected should be the smallest, most appropriate subset of the population for which decisions will be made based on the spatial or temporal boundaries.

***scavengers* (14.8.5):** See *collectors*.

***screening method* (6.5.5.3):** An economical gross measurement (alpha, beta, gamma) used in a tiered approach to method selection that can be applied to *analyte* concentrations below an *analyte* level in the *analytical protocol specifications* or below a fraction of the specified *action level.*

***secondary (outer) hydration sphere* (14.3.1):** See *hydration sphere*.

***self absorption* (6.4):** The absorption of nuclear particle or photon emissions within a matrix during the counting of a *sample* by a detector.

***sensitivity* (2.5.4.2):** (1) The ratio of the change in an output to the change in an input. (2) The term "sensitivity" is also frequently used as a synonym for "*detection capability*." See *minimum detectable concentration*.

***sensitivity analysis* (2.5.4):** Identifies the portions of the analytical protocols that potentially have the most impact on the decision.

***sensitivity coefficient* (19.4.3):** The *sensitivity coefficient* for an input estimate, x_i, used to calculate an output estimate, $y = f(x_1,x_2,\ldots,x_N)$, is the value of the partial derivative, $\partial f / \partial x_i$, evaluated at $x_1, x_2, \ldots, x_N$. The *sensitivity coefficient* represents the ratio of the change in y to a small change in x_i.

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***separation factor* (14.4.3):** In *ion-exchange chromatography*, the ratio of the distribution coefficients for two *ions* determined under identical experimental conditions. Separation factor (α) = $K_{d,1}/K_{d,2}$. The ratio determines the separability of the two *ions* by an ion-exchange system; separation occurs when $\alpha \neq 1$.

***serial correlation* (9.6.4.1):** When the characteristic of interest in a *sample* is more similar to that of samples adjacent to it than to samples that are further removed, the samples are deemed to be correlated and are not independent of each other (i.e., there is a *serial correlation* such that samples collected close in time or space have more similar concentrations than those samples further removed.).

***sigma* (σ) (3A.3):** The symbol σ and the term "sigma" are properly used to denote a true *standard deviation*. The term "sigma" is sometimes used informally to mean "*standard uncertainty*," and "*k*-sigma" is used to mean an *expanded uncertainty* calculated using the coverage factor *k*.

***significance level* (α) (6A.2):** In a *hypothesis test*, a specified upper limit for the probability of a *Type I decision error*.

***smears* (10.6.1):** See *swipes*.

***solid-phase extraction* (*SPE*) (14.4.5):** A *solvent* extraction system in which one of the liquid phases is made stationary by *adsorption* onto a solid support. The other phase is mobile (see *extraction chromatography*).

***solid-phase extraction membrane* (14.4.5):** A solid-phase extraction system in which the adsorbent material is embedded into a membrane producing an evenly distributed phase, which reduces the channeling problems associated with columns.

***solubility* (14.2.1):** The maximum amount of a particular *solute* that can be dissolved in a particular *solvent* under specified conditions (a *saturated solution*) without precipitating. *Solubility* may be expressed in terms of concentration, molality, mole fraction, etc.

***solubility equilibrium* (14.8.3.1):** The equilibrium that describes a solid dissolving in a *solvent* to produce a saturated solution.

***solubility-product constant* (14.8.3.1):** The equilibrium constant (K_{sp}) for a solid dissolving in a *solvent* to produce a saturated solution.

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***solute* (10.3.3.2):** The substance that dissolves in a *solvent* to form a solution. A *solute* can be a solid, liquid, or gas. In radiochemistry, it is commonly a solid or liquid.

***solution* (10.2.9):** A homogeneous mixture of one substance with another, usually a liquid with a gas or solid. The particles of the *solute* (molecules, atoms, or *ions*) are discrete and mix with particles of the *solvent* at the atomic, ionic, or molecular level.

***solvent* (10.2.9):** The substance that dissolves the *solute* to form a solution. The *solvent* can be a solid, liquid, or gas; but in radiochemistry, it is commonly a liquid.

***solvent extraction* (10.5.4.1):** A separation process that selectively removes soluble components from a mixture with a solvent. The process is based on the solubility of the components of the mixture in the *solvent* when compared to their solubility in the mixture. In liquid-liquid extraction, the process is based on an unequal distribution (partition) of the *solute* between the two immiscible liquids.

***source, radioactive* (3.3.4):** A quantity of material configured for radiation measurement. See also *calibration source*, *check source*, and *test source*.

***spatial variability* (2.5.2.2):** The nonuniformity of an *analyte* concentration over the total area of a site.

***specificity* (1.4.9):** See *method specificity*.

***spike* (1.4.8):** See *matrix spike*.

***spillover* (15.4.2.1):** See *crosstalk*.

***spurious error* (18.3.3):** A measurement error caused by a human blunder, instrument malfunction, or other unexpected or abnormal event.

***stability constant* (14.3.2):** See *formation constant.*

***stakeholder* (2.2):** Anyone with an interest in the outcome of a project. For a cleanup project, some of the *stakeholders* could be federal, regional, state, and tribal environmental agencies with regulatory interests (e.g., Nuclear Regulatory Commission or Environmental Protection Agency); states with have direct interest in transportation, storage and disposition of wastes, and a range of other issues; city and county governments with interest in the operations and safety at sites as well as economic development and site transition; and site advisory boards, citizens groups,

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licensees, special interest groups, and other members of the public with interest in cleanup activities at the site.

***standard deviation* (3A.3):** The *standard deviation* of a *random variable X*, denoted by σ_X, is a measure of the width of its *distribution*, and is defined as the positive square root of the *variance* of *X*.

***standard operating procedure* (*SOP*) (4.1):** Routine laboratory procedures documented for laboratory personnel to follow.

***standard reference material (SRM)* (6A.1):** A *certified reference material* issued by the National Institute of Standards and Technology (NIST) in the United States. A SRM is certified by NIST for specific chemical or physical properties and is issued with a certificate that reports the results of the characterization and indicates the intended use of the material.

***standard uncertainty* (1.4.7):** The uncertainty of a measured value expressed as an estimated *standard deviation*, often call a "1-sigma" (1-σ) uncertainty. The *standard uncertainty* of a value *x* is denoted by $u(x)$.

***statement of work* (*SOW*) (1.4.11):** The part of a *request for proposals*, contract, or other agreement that describes the project's scope, schedule, technical specifications, and performance requirements for all radioanalytical laboratory services.

***stationary phase* (14.7.4.1):** The phase in a chromatographic system that is not moving with respect to the mobile phase. The *stationary phase* can be a solid, a nonvolatile liquid coated onto an inert matrix, or a substance trapped in an inert matrix.

***statistical control* (1.4.8):** The condition describing a process from which all special causes have been removed, evidenced on a *control chart* by the absence of points beyond the *control limits* and by the absence of nonrandom patterns or trends within the *control limits*. A special cause is a source of variation that is intermittent, unpredictable, or unstable. See *control chart*, *in control*, and *control limits*.

***statistical parameter* (2.5, Table 2.1):** A quantity used in describing the probability distribution of a *random variable*" (ISO, 1993b).

***statistical test* (4.6.2.3):** A statistical procedure to decide whether a *null hypothesis* should be rejected in favor of the *alternative hypothesis* or not rejected." This also can be called a *hypothesis test*.

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***subsample* (12.3.1.4):** (1) A portion of a *sample* removed for testing. (2) To remove a portion of a *sample* for testing.

***subsampling factor* (19.5.12):** As used in MARLAP, a variable, F_S, inserted into the mathematical model for an analytical measurement to represent the ratio of the *analyte* concentration of the subsample to the *analyte* concentration of the original *sample*. The *subsampling factor* is always estimated to be 1 but has an uncertainty that contributes to the combined *standard uncertainty* of the measured result.

***surface adsorption* (14.8.3.3, Table 14.12):** (1) *Adsorption* of particles of a substance onto the surface of another substance. (2) A mechanism of *coprecipitation* in which *ions* are adsorbed from solution onto the surfaces of precipitated particles.

***survey* (2.3.2):** "An evaluation of the radiological conditions and potential hazards incident to the production, use, transfer, release, disposal, or presence of radioactive materials or other sources of radiation. When appropriate, such an evaluation includes the a physical survey of the location of radioactive material and measurements or calculations of levels of radiation, or concentrations of quantities of radioactive material present" (Shleien, 1992). A *survey* is a semiquantitative measure of the gross radiological conditions of a material or area (for dose and contamination). A *screen* is a qualitative assessment to determine the type of *radionuclides* (alpha, beta, gamma) and the relative amount (high, medium, low) of each that might be present.

***survey unit* (2.5.2.4):** A geographical area consisting of structures or land areas of specified size and shape at a remediated site for which a separate decision will be made whether the unit attains the site-specific reference-based cleanup standard for the designated pollution parameter. *Survey units* are generally formed by grouping contiguous site areas with a similar use history and the same classification of contamination potential. *Survey units* are established to facilitate the survey process and the statistical analysis of survey data. (MARSSIM, 2000)

***suspension* (10.3.3.2):** A mixture in which small particles of a solid, liquid, or gas are dispersed in a liquid or gas. The dispersed particles are larger than colloidal particles and produce an opaque or turbid mixture that will settle on standing by gravity and be retained by paper filters. See *colloids* and *colloidal solution*.

***swipes* (10.6.1):** A filter pad used to determine the level of general radioactive contamination when it is wiped over a specific area, about 100 cm^2 in area. Also called *smears* or wipes.

***systematic effect* (3A.4):** Any effect in a measurement process that does not vary randomly when the measurement is repeated.

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***systematic error* (3A.4):** The mean value that would result from an infinite number of measurements of the same *measurand* carried out under repeatability conditions minus a true value of the *measurand* (ISO, 1993a).

***systematic planning process* (1.4.2):** See *directed planning process*.

***target analyte* (3.3.1):** A *radionuclide* on the *target analyte list*. Also called *radionuclide of interest* or "radionuclide of concern." See *analyte*.

***target analyte list* (3.3.1):** A list of the *radionuclides* of concern for the project.

***target radionuclide* (18.4.1):** See *radionuclide of interest*.

***technical evaluation committee* (*TEC*) (5.3.9):** A team of technical staff members that assists in the selection of a contract laboratory by reviewing proposals and by auditing laboratory facilities.

***technical proposal* (5.5.1.):** A document, submitted by a laboratory bidding on a contract, which addresses all of the technical and general laboratory requirements within a *request for proposals* and *statement of work*.

***temporal trend* (2.5, Table 2.1):** Effects that time have on the *analyte* concentration in the matrix or *sample*. The *temporal boundaries* describe the time frame the study data will represent (e.g., possible exposure to local residents over a 30-year period) and when samples should be taken (e.g., instantaneous samples, hourly samples, annual average based on monthly samples, samples after rain events).

***tests of detection* (8.3.1):** *Tests of detection* determine the presence or absence of *analytes*. Normally, only numerous *quality control* exceptions and failures in one or more of the *tests of detection* and uncertainty are sufficient reason to reject data.

***tests of unusual uncertainty* (8.3.1):** Part of the validation plan that specifies the level of *measurement uncertainty* considered unusually high and unacceptable.

***test source* (14.10.9.7):** The final radioanalytical processing product or matrix (e.g., precipitate, solution, filter) that is introduced into a measurement instrument. A *test source* is prepared from laboratory sample material for the purpose of determining its radioactive constituents. See *calibration source*, *check source*, and *source, radioactive*.

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***thin-layer chromatography* (14.7.3):** A chromatographic process in which a thin layer of a *stationary phase* in coated onto a solid support such as a plastic or glass plate. The stationary material is an absorbing solid and the mobile phase is a liquid.

***tolerable decision error rates* (2.3.3):** The limits on *decision error rates* that will be acceptable to the *stakeholder*/customer.

***tolerance limit* (18.3.3):** A value, that may or may not have a statistical basis, which is used as the measure of acceptable or unacceptable values. A *tolerance limit* is sometimes referred to as a "Go/No Go" limit. See *warning limit*, *control chart*.

***total effective dose equivalent* (*TEDE)* (2.5.2.1):** The sum of the effective dose equivalent (for external exposure) and the committed effective dose equivalent (for internal exposure). TEDE is expressed in units of sievert (Sv) or rem (MARSSIM, 2000). See *action level*, *dose equivalent*, and *total effective dose equivalent*.

***total propagated uncertainty* (*TPU)* (19.2):** See *combined standard uncertainty*, which is the preferred term.

***traceability* (8.5.1.5):** "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" (ISO, 1993a).

***tracer* (1.4.8):** See *radiotracer*.

***Type A evaluation (of uncertainty)* (19.3.3):** "Method of evaluation of uncertainty by the statistical analysis of series of observations" (ISO, 1995).

***Type B evaluation (of uncertainty)* (19.3.3):** "Method of evaluation of uncertainty by means other than the statistical analysis of series of observations" (ISO, 1995); any method of uncertainty evaluation that is not a Type A evaluation.

***Type I decision error* (2.5.3):** In a hypothesis test, the error made by rejecting the null hypothesis when it is true. A *Type I decision error* is sometimes called a "*false rejection*" or a "*false positive*."

***Type II decision error* (2.5.3):** In a hypothesis test, the error made by failing to reject the null hypothesis when it is false. A *Type II decision error* is sometimes called a "*false acceptance*" or a "*false negative*."

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***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).

***uncertainty interval* (19.3.6):** The interval from $y - U$ to $y + U$, where y is the measured result and U is its *expanded uncertainty*.

***uncertainty propagation* (19.1):** Mathematical technique for combining the *standard uncertainties* of the input estimates for a mathematical model to obtain the combined *standard uncertainty* of the output estimate.

***uncertainty propagation formula (first-order)* (19.4.3):** the generalized mathematical equation that describes how standard uncertainties and *covariances* of input estimates combine to produce the combined *standard uncertainty* of an output estimate. When the output estimate is calculated as $y = f(x_1, x_2, ..., x_N)$, where f is a differentiable function of the input estimates $x_1, x_2, \ldots, x_N$, the uncertainty propagation formula may be written as follows:

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

This formula is derived by approximating the function $f(x_1, x_2, ..., x_N)$ by a first-order Taylor polynomial. In the *Guide to the Expression of Uncertainty of Measurement*, the uncertainty propagation formula is called the "law of propagation of uncertainty" (ISO, 1995).

***unsaturated solution* (14.8.2):** A solution whose concentration of *solute* is less than that of a saturated solution. The solution contains less *solute* than the amount of *solute* will dissolve at the temperature of the solution, and no solid form of the *solute* is present.

***validation* (1.1):** See *data validation*.

***validation criterion* (2.5.4.2):** Specification, derived from the *measurement quality objectives* and other analytical requirements, deemed appropriate for evaluating data relative to the project's analytical requirements. Addressed in the *validation plan*.

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***validation flags* (1.4.11):** Qualifiers that are applied to data that do not meet the acceptance criteria established to assure data meets the needs of the project. See also *data qualifier*.

***validation plan* (2.7.4.2):** An integral part of the initial planning process that specifies the data deliverables and *data qualifiers* to be assigned that will facilitate the *data quality assessment*.

***variance* (9.6.2.3):** The *variance* of a *random variable X*, denoted by Var(X), σ_X^2, or $V(X)$, is defined as $E[(X - \mu_X)^2]$,where μ_X denotes the mean of X. The *variance* also equals $E(X^2) - \mu_X^2$.

***verification* (1.2):** See *data verification.*

***volatility* (10.3.4.1):** The tendency of a liquid or solid to readily become a vapor (evaporates or sublimes) at a given temperature. More volatile substances have higher vapor pressures than less volatile substances.

***volatilization* (10.3.3.2, Table 10.1):** A separation method using the volatility of liquids or solids to isolate them from nonvolatile substances, or to isolate a gas from a liquid.

***warning limit* (3.3.7.3):** Predetermined values plotted on a *control chart* between the central line and the *control limits*, which may be used to give an early indication of possible problems with the monitored process before they become more significant. The monitored variable will occasionally fall outside the warning limits even when the process is *in control*; so, the fact that a single measurement has exceeded the warning limits is generally not a sufficient reason to take immediate corrective action. See *tolerance limit*.

***weight distribution coefficient* (14.7.4.1):** In *ion-exchange chromatography*, the ratio of the weight of an *ion* absorbed on one gram of dry ion-exchange *resin* to the weight of the *ion* that remains in one milliliter of solution after equilibrium has been established. The ratio is a measure of attraction of an *ion* for a *resin*. Comparison of the weight distribution coefficient for *ions* in an analytical mixture is a reflection of the ability of the ion-exchange process to separate the *ions* (see *separation factor*).

***Welch-Satterthwaite formula* (19C.2):** An equation used to calculate the *effective degrees of freedom* for the combined *standard uncertainty* of an output estimate when the number of degrees of freedom for the *standard uncertainty* of each input estimate is provided (ISO, 1995).

***work plan* (1.6.1):** The primary and integrating plan document when the data collection activity is a smaller supportive component of a more comprehensive project. The *work plan* for a site investigation will specify the number of samples to be collected, the location of each *sample*, and

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the analyses to be performed. A newer concept is to develop a *dynamic work plan* that specifies the decisionmaking logic used to determine where the samples will be collected, when the sampling will stop, and what analyses will be performed, rather than specify the number of samples to be collected and the location of each sample.

***year*:** (1) Mean solar or tropical year is 365.2422 days (31,556,296 seconds) and is used for calculations involving *activity* and *half-life* corrections. (2) Calendar year, i.e., 12 months, is usually used in the regulatory sense when determining compliance.

***yield* (1.6.2):** The ratio of the amount of *radiotracer* or *carrier* determined in a sample analysis to the amount of *radiotracer* or *carrier* originally added to a *sample*. The yield is an estimate of the *analyte* during analytical processing. It is used as a correction factor to determine the amount of *radionuclide* (*analyte*) originally present in the sample. *Yield* is typically measured gravimetrically (via a *carrier*) or radiometrically (via a *radiotracer*). Compare with *recovery*.

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11. ABSTRACT *(200 words or less)*

The Multi-Agency Radiological Laboratory Analytical Protocols (MARLAP) manual provides guidance for the planning, implementation, and assessment of projects that require the laboratory analysis of radionuclides. MARLAP's goal is to provide guidance for project planners, managers, and laboratory personnel to ensure that radioanalytical laboratory data will meet a project's or program's data requirements. The manual offers a framework for national consistency in the form of a performance-based approach for meeting data requirements that is scientifically rigorous and flexible enough to be applied to a diversity of projects and programs. The guidance in MARLAP is designed to help ensure the generation of radioanalytical data of known quality, appropriate for its intended use. Examples of data collection activities that MARLAP supports include site characterization, site cleanup and compliance demonstration, decommissioning of nuclear facilities, emergency response, remedial and removal actions, effluent monitoring of licensed facilities, environmental site monitoring, background studies, and waste management activities.

MARLAP is organized into two parts. Part I, Volume 1, is intended for project planners and managers, provides the basic framework of the directed planning process as it applies to projects requiring radioanalytical data for decision making. Part II, Volumes 2 and 3, is intended for laboratory personnel.

12. KEY WORDS/DESCRIPTORS *(List words or phrases that will assist researchers in locating the report.)*

Multi-Agency Radiological Laboratory Analytical Protocols, MARLAP, radiological , laboratory, laboratory sample, analytical protocols, performance-based approach, planning, measurement, quality assurance, survey(s), decommissioning, statistics, waste management, radioanalytical laboratory services, data validation, data quality assessment, data collection

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