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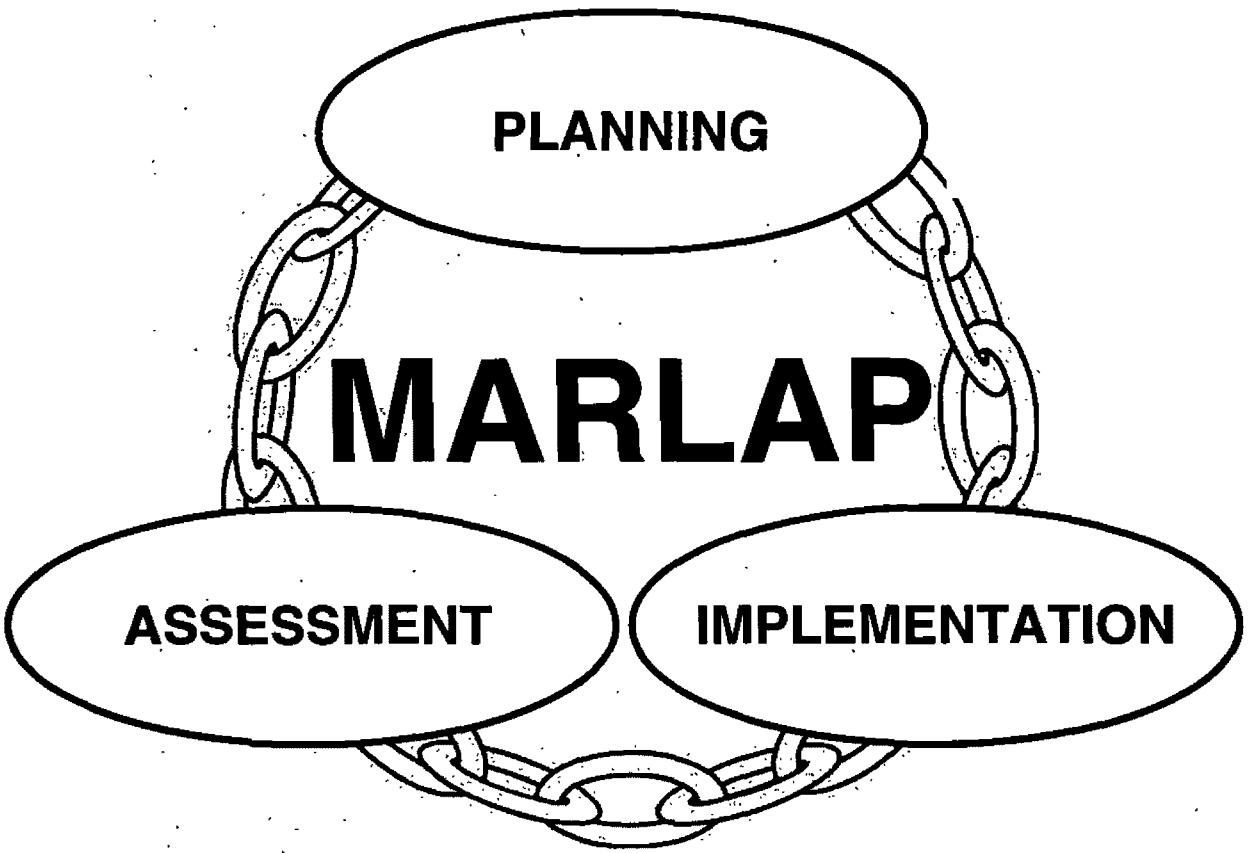
Multi-Agency Radiological Laboratory Analytical Protocols Manual

Volume II: Chapters 10 – 20 and Appendices



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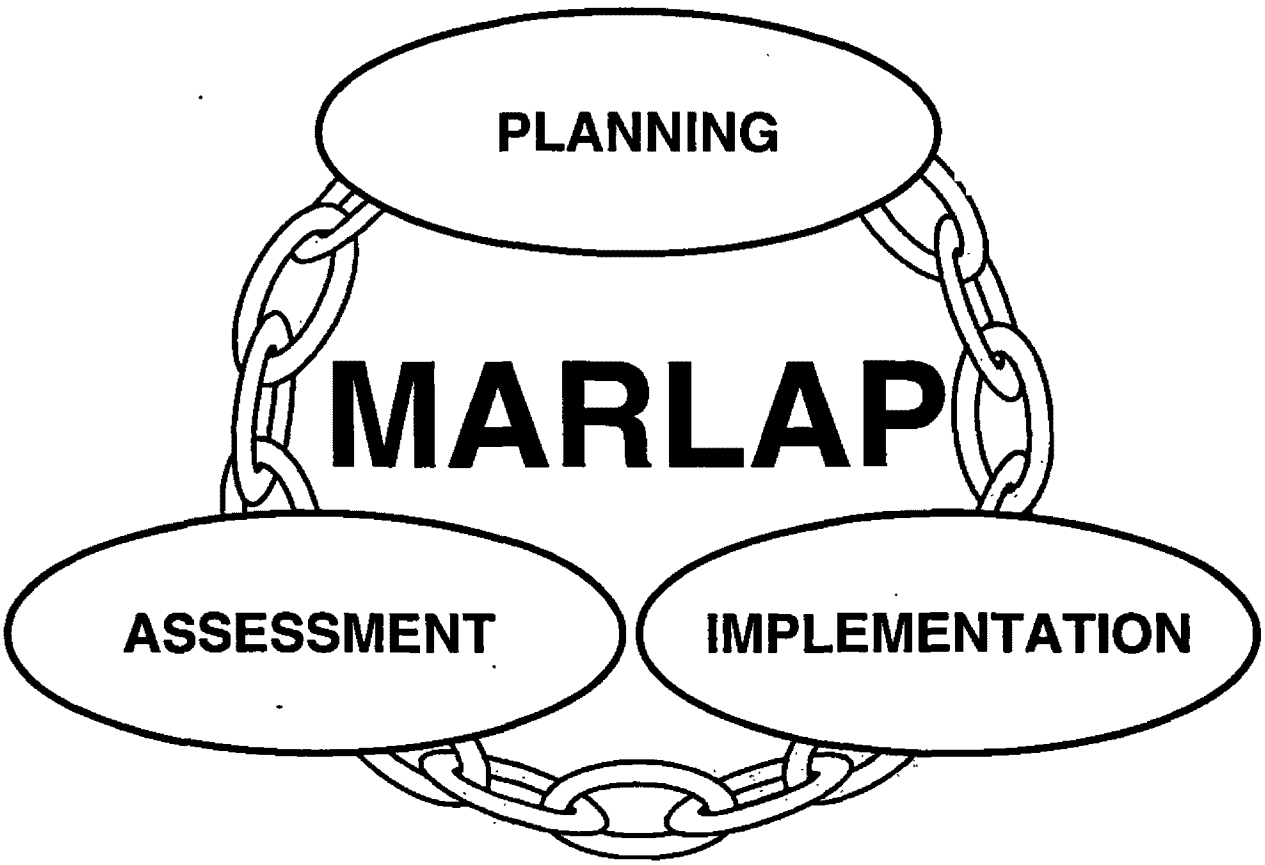

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10 FIELD AND SAMPLING ISSUES THAT AFFECT LABORATORY MEASUREMENTS

Part I: Generic Issues

10.1 Introduction

The primary purpose of this chapter is to provide guidance on issues that affect laboratory measurements to project planners and managers tasked with developing a field sampling plan. Specifically, this chapter provides guidance on activities conducted primarily after the proper collection of the sample. Sampling design and collection are beyond the scope of MARLAP. A field sampling plan should be a comprehensive document that provides detailed guidance for collecting, preparing, preserving, shipping, tracking field samples, and recording field data. The principal objective of a well-designed sampling plan is to provide representative samples of the proper size for analysis. Critical to the sampling plan are outputs of the systematic planning process, which commonly define the Analytical Protocol Specifications (APS) and the Measurement Quality Objectives (MQO) that must be met. While a comprehensive discussion that extends to field sampling strategies is beyond the scope of this chapter, specific aspects of sample collection methods and physical preparation and preservation of samples warrant further discussion because they impact the analytical process and the data quality.

This chapter is divided into two main parts. Part I identifies general elements of a field sampling plan and provides project planners with general guidance. Part II provides more detailed information. Matrix-specific guidance and technical data are presented for liquid, solid, airborne, and surface contaminants requiring field sampling. This information will assist project planners further in the development of standard operating procedures (SOPs) and training for field personnel engaged in preparation and preservation of field samples.

The need to specify sample collection methods, and preparation and preservation of field samples, is commonly dictated by one or more of the following:

- The systematic planning process that identifies the type, quality, and quantity of data needed to satisfy a decision process;
- The potential alteration of field samples by physical, chemical, and biological processes during the time between collection and analysis;
- Requirements specified by the analytical laboratory pertaining to sample analysis;
- Requirements of analytical methods; and
- Requirements of regulators (e.g., Department of Transportation).

10.1.1 The Need for Establishing Channels of Communication

Of critical importance to the effective design of a sampling plan are the input and recommendations of members representing: (1) the field sampling team; (2) the health physics professional staff; (3) the analytical laboratory; (4) statistical and data analyses; (5) quality assurance personnel, and (6) end-users of data.

Beyond the initial input that assist the project planners in the design of the sampling plan, it is equally important to maintain open channels of communication among key members of the project team throughout the process. For example, the analytical laboratory should be provided with contacts from the field sampling team to ensure that modifications discrepancies and changes are addressed and the timely resolution of potential problems.

Communication among project staff, field personnel, and the laboratory offer a means to coordinate activities, schedules, and sample receipt. Project planning documents generated from the systematic planning process, such as APS and statements of work (SOWs), should be consulted, but they cannot address all details. Additional communication likely will be necessary. Communication conveys information about the number and type of samples the laboratory can expect at a certain time. Documentation with special instructions regarding the samples should be received before the samples arrive. This information notifies the laboratory of any health and safety concerns so that laboratory personnel can implement proper contamination management practices. Health and safety concerns may affect analytical procedures, sample disposition, etc. The analytical laboratory should have an initial understanding about the relative number of samples that will be received and the types of analyses that are expected for specific samples. Furthermore, advance communications allow laboratory staff to adjust to modifications, discrepancies, and changes.

10.1.2 Developing Field Documentation

The field organization must conduct its operations in such a manner as to provide reliable information that meets the data quality objectives (DQOs). To achieve this goal, all relevant procedures pertaining to sample collection and processing should be based on documented standard operating procedures that include the following activities:

- Developing a technical basis for defining the size of individual samples;
- Selecting field equipment and instrumentation;
- Using proper sample containers and preservatives;
- Using consistent container labels and sample identification codes;
- Documenting field sample conditions and exceptions;
- Documenting sample location;
- Tracking, accountability and custody, and shipment forms;

- Legal accountability, such as chain-of-custody record, when required;
- Selecting samples for field QC program;
- Decontaminating equipment and avoiding sample cross-contamination;
- Sample packaging, shipping, and tracking; and
- Health and safety plan.

10.2 Field Sampling Plan: Non Matrix Specific Issues

10.2.1 Determination of Analytical Sample Size

When collecting environmental samples for radioanalysis, an important parameter for field personnel is the mass, volume, or weight of an individual sample that must be collected. The required minimum sample size is best determined through the collective input of project planners, field technicians, and laboratory personnel who must consider the likely range of the contaminant concentrations, the type of radiation emitted by constituents or analytes (α, β, γ), field logistics, and the radioanalytical methods that are to be employed. For samples to yield useful data, it is important to have a quantitative understanding of the relationship between sample size and project specific requirements.

10.2.2 Field Equipment and Supply Needs

Before starting field sampling activities, all necessary equipment and supplies should be identified, checked for proper operation and availability, and—when appropriate—pre-assembled. Instrumentation and equipment needs will depend not only on the medium to be sampled, but also on the accessibility of the medium and the physical and chemical properties of radionuclide contaminants under investigation.

Independent of specialized field equipment and instrumentation, field sampling supplies commonly include the following:

- Sampling devices (e.g., trowel, hand auger, soil core sampler, submersible water pump, high volume air filter, etc.);
- Sampling preparation equipment (e.g., weighing scales, volume measuring devices, soil screening sieves, water filtering equipment, etc.);
- Sample preservation equipment and agents (e.g., refrigeration, ice, formaldehyde or acid additives);
- Personnel protective gear (e.g., respiratory protective devices, protective clothing such as gloves and booties, life-preservers, etc.);

- Proper writing utensils (e.g., permanent pens and markers);
- Field logbooks and field tracking forms;
- Maps, distance measuring equipment, global positioning systems, or other location-determining equipment;
- Field sampling flags or paint;
- Chain-of-custody (COC) forms;
- Sample tags, labels, documents;
- Appropriately labeled sample containers;
- Shipment containers and packing materials that meet DOT regulations;
- Shipment forms;
- Analysis request form identifying the type of radioanalysis to be performed; and
- Health and Safety Plan requirements (medical kit, etc.).

10.2.3 Selection of Sample Containers

There are several physical and chemical characteristics that must be considered when selecting a suitable container for shipping and storing samples. Important characteristics include the container material and its size, configuration, and method for ensuring a proper seal.

10.2.3.1 Container Material

Sample containers must provide reasonable assurance of maintaining physical integrity (i.e., against breakage, rupture, or leakage) during handling, transport, and potentially long periods of storage. The most important factor to consider in container selection is the chemical compatibility between container material and sample. Containers may include ordinary bottle glass, borosilicate glass (such as Pyrex or Corex), plastics (e.g., high density polyethylene—HDPE), low density polyethylene, polycarbonate, polyvinyl chloride (PVC), fluorinated ethylene propylene (Reflon), or polymethelpentene. For select samples, the choice of containers may require metal construction or be limited to paper envelopes.

124 10.2.3.2 Container Opening and Closure

125 Selection of a suitable container also must consider the ease with which the sample is introduced
126 into the container. For example, a wide-mouthed container will provide easier access for the
127 introduction and withdrawal of sample material and eliminate spills or the need for additional
128 tools or equipment (e.g., funnel) that may become a source of cross contamination among
129 samples.

130 Equally important is the container closure or seal. As a rule, snap-on caps should not be
131 considered for liquid samples because they do not ensure a proper seal. Even when screw caps
132 are used, it is frequently prudent to protect against vibration by securing the cap with electrical or
133 duct tape. A proper seal is important for air samples, such as radon samples. The container cap
134 material, if different from the container material, must be equally inert with regard to sample
135 constituents.

136 10.2.3.3 Sealing Containers

137 Tamper-proof seals offer an additional measure to ensure sample integrity. A simple example
138 includes placing a narrow strip of paper over a bottle cover and then affixing this to the container
139 with a wide strip of clear tape (EPA, 1987, Exhibit 5-6, example of custody seals). The paper
140 strip can be initialed and dated in the field to indicate the staff member who sealed the sample
141 and the date of the seal. Individually sealing each sample with a custody seal with the collector's
142 initials and the date the sample was sealed may be required by the project. The seal ensures legal
143 defensibility and integrity of the sample at collection. Tamper-proof seals should only be applied
144 once field processing and preservation steps are completed. Reopening this type of sealed
145 container in the field might warrant using a new container or collecting another sample.

146 10.2.3.4 Precleaned and Extra Containers

147 The reuse of sample containers is discouraged because traces of radionuclides might persist from
148 initial container use to subsequent use. The use of new containers for each collection removes
149 doubts concerning radionuclides from previous sampling. New containers might also require
150 cleaning (ASTM D5245) to remove plasticizer used in container production or to pretreat glass
151 surfaces. Retaining extra empty containers from a new lot or a special batch of precleaned and
152 treated containers offers the laboratory container blanks for use as part of quality control. Extra
153 containers are also useful for taking additional samples as needed during field collection and to
154 replace broken or leaking containers.

155 **10.2.4 Container Label and Sample Identification Code**

156 Each sample can only be identified over the life of a study if a form of *permanent identification*
157 is provided with or affixed to the container or available in sample log. The most useful form of

identification utilizes a *unique identifier* for each sample. Such unique identification codes ensure the project's ability to track individual samples. The standard operating procedure (SOP) that addresses sample identification should describe the method to be used to assure that samples are properly identified and controlled in a consistent manner. Containers sometimes may be pre-labeled with identification numbers already in place.

Any identification recorded on a container or a label affixed to the container should remain with the container throughout sample processing and storage. The identification information should be written with a permanent marker—especially if the labels are exposed to liquids. Information can be recorded directly on the container or on plastic or paper tags securely fixed to the container. However, tags are more likely to become separated from containers than are properly secured labels.

Labels, tags, and bar codes should be rugged enough so no information is lost or compromised during field work, sample transport, or laboratory processing. Transparent tape can be used to cover the label once it is completed. The tape protects the label, adds moisture resistance, prevents tampering with the sample information, and helps secure the label to the container.

The project manager needs to determine if a sample number scheme may introduce bias into the analysis process. That is, the lab may be aware of trends or locations from the sample identification and this could influence their judgment as to the anticipated result and thereby introduce actions on the part of lab personnel that they would not otherwise take. The project manager needs to determine the applicability of electronic field data recorders and the issue of electronic signatures for the project.

A unique identifier can include a code for a site, the sample location at the site, and a series of digits identifying the year and day of year (e.g., "1997-127" uses the Julian date, and "062296" describes a month, day, and year). Alternatively, a series of digits can be assigned sequentially by site, date, and laboratory destination. The use of compass headings and grid locations also provides additional unique information (e.g., "NW fence, sampled at grid points: A1 through C25, 072196, soil"). With this approach, samples arriving at a laboratory are then unique in two ways. First, each sample can be discriminated from materials collected at other sites. Second, if repeat samples are made at a single site, then subsequent samples from the same location are unique only by date. Labeling of samples sequentially might not be appropriate for all studies. Bar coding may reduce transcription errors and should be evaluated for a specific project.

10.2.5 Field Data Documentation

All information pertinent to field sampling is documented in a log book or on a data form. The log book should be bound and the pages numbered consecutively and forms should be page-numbered and dated. Where the same information is requested routinely, preprinted log books or data sheets will minimize the effort and will standardize the presentation of data. Even when

194 standardized preprinted forms are used, all information recorded should be in indelible ink, with
195 all entry errors crossed out with a single line and initialed. The color of ink used should be
196 compatible with the need to copy that information. All entries should be dated and signed on the
197 date of entry. Initials should be legible and traceable, so that it is clear who made the entry.

198 Whenever appropriate, log or data form entries should contain—but are not limited to—the
199 following:

200 • Identification of Project Plan or Sampling Plan;

201 • Location of sampling (e.g., reference to grid location, maps, photographs, location in a
202 room);

203 • Date and time of sample collection;

204 • Sample medium (e.g., surface water, soil, sediment, sludge, etc.);

205 • Suspected radionuclide constituents;

206 • Sample-specific ID number;

207 • Sample volume, weight, depth;

208 • Sample type (e.g., grab, composite);

209 • Sample preparation used (e.g., removal of extraneous matter);

210 • Sample preservation used;

211 • Requested analyses to be performed (e.g., gross beta/gamma, gamma spectroscopy for a
212 specific radionuclide, radiochemical analysis);

213 • Sample destination including name and address of analytical laboratory;

214 • Names of field persons responsible for collecting sample;

215 • Physical and meteorological conditions at time of sample collection;

216 • Special handling or safety precautions;

- Recommendations regarding time to date of analysis that reflect (1) the loss of radioactivity due to natural decay, (2) the ingrowth and secular equilibrium of short-lived progeny, or (3) the potential loss of radioactivity due to evaporation or volatility; and

- Signatures or initials of appropriate field personnel. When using initials, ensure that they can be uniquely identified with an individual.

Labels affixed to individual sample containers should contain key information that is an abstract of log book data sheets. When this is not practical, a copy of individual sample data sheets may be included along with the appropriately ID-labeled sample.

10.2.6 Field Tracking, Custody, and Shipment Forms

A sample tracking procedure must be in place for all projects in order that the proper location and identification of samples is maintained throughout the process from collection through handling, preservation, storage, transfer to laboratory, and disposal. The term "tracking," when used here, connotes a tracking and accountability process that meets generally acceptable laboratory practices as described by accrediting bodies, but is less stringent than a formal chain-of-custody process. Tracking also develops a record of all individuals responsible for the custody and transfer of the samples. Chapter 4 (*Project Plan Documents*) discusses the process of tracking and accountability. Also, Chapter 11 (*Sample Receipt, Inspection, and Tracking*) discusses the laboratory process of tracking.

When transferring the possession of samples, the individuals relinquishing and the individuals receiving the samples should sign, date, and note the time on the form. A standardized form should be designed for recording tracking or formal chain-of-custody information related to tracking sample possession. If samples are to be split and distributed to more than one analytical laboratory, multiple forms will be needed to accompany sample sets. The sample collector is responsible for initiating the sample tracking record. The following information is considered minimal for sample tracking:

- Name of project;
- Sampler's signature;
- Sample ID;
- Sample location
- Date and time sampled;
- Sample type;
- Preservatives;
- Number of containers;
- Analysis required;
- Signatures of persons relinquishing, receiving, and transporting the samples;
- Signature for laboratory receipt;

- Method of shipment or carrier and air bill when shipped or shipping manifest identification upon receipt; and
- Comments regarding the integrity of shipping container and individual samples.

10.2.7 Chain of Custody

The legal portion of the tracking and handling process that ensures legal defensibility from sample collection to data reporting has become relatively standardized and is referred to as the chain-of-custody (COC) process (APHA, 1996). Guidance is provided in "Standard Practice for Sampling Chain-of-Custody Procedures" (ASTM D4840) and NIOSH (1983). The level of security required to maintain an adequate chain of custody is that necessary to establish a "reasonable probability" that the sample has not been tampered with. For court proceedings, the requirements are established in law. COC procedures are important in demonstrating sample control when litigation is involved. In many cases, Federal, State or local agencies may require that COC be maintained for specific projects. COC is usually not required for samples that are generated and immediately tested within a facility or continuous (rather than discrete or integrated) samples that are subject to real- or near-real-time analysis (e.g., continuous screening).

When COC is required, the custody information is recorded on a COC form. Chain-of-custody documents vary by organization. Communication between field and laboratory personnel is critical to the successful use of COC. Any error made on a custody form is crossed out with a single line and dated and initialed. Use of correction ink or obliteration of data is not acceptable. Inform the laboratory when COC is required before the samples are received (see Section 11.2 for further information). The COC documents are signed by personnel who collect the samples. A chain-of-custody record accompanies the shipment and one or more copies are distributed to the project coordinator or other office(s) where field and laboratory records are maintained. An example of a COC form is shown in Figure 10.1. Additional information and examples of custody forms are illustrated by EPA (1987) and EPA (1994).

10.2.8 Field Quality Control

A project plan should have been developed to ensure that all data are accurate and that decisions based on these data are technically sound and defensible. The implementation of a project plan requires quality control (QC) procedures. QC procedures, therefore, represent specific tools for measuring the degree to which quality assurance objectives are met. Field quality control measures are comprehensively discussed in ASTM D5283.

While some types of quality control (QC) samples are used to assess analytical process, field quality control samples are used to assess the actual sampling process. The type and frequency of these field QC samples must be specified by the project planning process along with being included in the project planning documents and identified in the sampling plan. Definitions for

CHAIN-OF-CUSTODY RECORD

FIELD IDENTIFICATION NUMBER	FIELD LOCATION	DATE	TIME	SAMPLERS (Signature)					
				SAMPLE MATRIX			SEQ. No.	No. of Containers	Analysis Required
				Water	Soil	Air			
Relinquished by: (Signature)				Received by: (Signature)					Date/Time /
Relinquished by: (Signature)				Relinquished by: (Signature)					Date/Time /
Relinquished by: (Signature)				Received by: (Signature)					Date/Time /
Received by: (Signature)				Received by Laboratory for field analysis: (Signature)					Date/Time /
Dispatched by: (Signature)		Date		Time	Received for Laboratory by:				Date/Time /
Method of Shipment:									
Distribution: Orig. - Accompany Shipment 1 Copy – Survey Coordinator Field Files									

FIGURE 10.1—Example of chain-of-custody record.

certain types of field QC samples can be found in ASTM D5283 and MARSSIM (2000).

10.2.9 Decontamination of Field Equipment

Sampling SOPs must describe the recommended procedure for cleaning field equipment before and during the sample collection process, as well as any pretreatment of sample containers. The SOPs should include the cleaning materials and solvents used, the purity of rinsing solution or water, the order of washing and rinsing, associated personnel safety precautions, and the disposal of cleaning agents.

Detailed step-by-step procedures for the decontamination of field equipment used in the sampling of low-activity soils, soil gas, sludges, surface water, and ground water are given in ASTM D5608.

10.2.10 Packing and Shipping

The final responsibility of field sampling personnel is to properly prepare and package samples for transport or shipment by a commercial carrier. All applicable State and Federal shipping requirements, as discussed later in this section, must be followed. Samples transported over shorter distances by the sampling or testing agency by way of automobile, van, or truck will require less stringent packing requirements. In most instances, placing sealed sample containers within cardboard boxes (or similar containers) in which individual samples are sufficiently cushioned to guard against bumping, rolling, or dropping, is adequate.

When samples must be shipped by way of a commercial carrier or the U.S. Postal Service, containers must be designed to protect samples against crushing forces, impacts, and severe temperature fluctuations. Within each shipping container, the cushioning material (sawdust, rubber, polystyrene, urethane foam, or material with similar resiliency) should encase each sample completely. The cushioning between the samples and walls of the shipping containers should have a minimum thickness of one inch. A minimum thickness of two inches should be provided on the container floor.

Consideration must also be given to protect samples against potentially adverse impacts of temperature fluctuations. When appropriate, sample protection against freezing, thawing, sublimation, evaporation, or extreme temperature variation may require that the entire interior surface of the shipping container be lined with an adequate layer of insulation. In many instances, the insulating material may also serve as the cushioning material.

When metal containers are used, the requirements for container security, cushioning, and insulation apply equally. For smaller volume and low-weight samples, properly lined containers constructed with laminated fiberboard, plastic, or reinforced cardboard outer walls also may be used.

When samples are shipped as liquids in glass or other breakable sample containers, additional packaging precautions may have to be taken. Additional protection is obtained when sample containers are shipped in nested containers, in which several smaller containers (i.e., inner containers) are packed inside a second larger container (i.e., the outer pack or overpack). To contain any spills of sample material within the shipping container, it is advisable either to wrap individual samples or to line the shipping container with absorbent material, such as asbestos-free vermiculite or pearlite.

For proper packaging of liquid samples, additional guidance has been given by EPA (1987) and includes the following:

- All sample bottles are taped closed;
- Each sample bottle is placed in a plastic bag and the bag is sealed;
- Each sample bottle may be placed in a separate metal can filled with vermiculite or other packing material, then the lid may be fixed to the can with tape;
- The cans are placed upright in a cooler that has its drain plug taped closed, inside and out, and lined with a plastic bag; and
- The cooler is filled with packing material—"bubble wrap" or cardboard separators may be used—and closed with sealing tape.

Field screening measurements are made for compliance with Department of Transportation regulations, 49 CFR Parts 170 through 189, as well as compliance with the laboratory's U.S. NRC (10 CFR Part 71) and Agreement State license. International requirements may also apply. See International Air Transport Association (IATA) Dangerous Goods Regulations for additional guidance. These regulations not only set contamination and dose limits for shipping containers, but also describe the types of containers and associated materials that are to be used based on the total activity and quantity of materials shipped. When the samples are screened in the field with survey instrumentation, the results should be provided to the laboratory. This information should also state the distance used from the probe to the packing container wall. Measurements normally are made in contact or at one meter. The readings in contact are most appropriate for laboratory use. The screening measurements in the field are mainly for compliance with transportation requirements and are usually in units of exposure. Laboratory license requirements are usually by isotope and activity. Project planning and communication are essential to ensure that a specific set of samples can be transported, received, and analyzed safely while complying with applicable rules and regulations.

The external surface of each shipping container must be labeled clearly, contain information regarding the sender and receiver, and should include the respective name and telephone number of a contact. When required, proper handling instructions and precautions should be clearly marked on shipping containers. Copies of instructions, shipping manifest or container inventory, chain of custody, and any other paperwork that is enclosed within a shipping container should be safeguarded by placing documents within a sealed protected envelope.

10.2.11 Worker Health and Safety Plan

In some cases, field samples will be collected where hazardous agents or site conditions might pose health and safety considerations for field personnel. These can include chemical, biological, and radiological agents, as well as common industrial hazards associated with machinery, noise levels, and heat stress. The health and safety plan established in the planning process should be

followed. For the Department of Defense (DOD), these plans may include imminent threats to life, such as unexploded ordnance, land mines, hostile forces, chemical agents, etc.

10.2.11.1 Physical Hazards

MECHANICAL EQUIPMENT

Personnel working with hand-held tools (e.g., sledge hammers used for near-surface coring) or power tools and equipment are subject to a variety of hazards. For example, personnel drilling monitoring wells are exposed to a variety of potential mechanical hazards, including moving machinery, high-pressure lines (e.g., hydraulic lines), falling objects, drilling through underground utilities, flying machinery parts, and unsafe walking and working surfaces. The consequences of accidents involving these physical hazards can range from minor to fatal injury.

At a minimum, workers should be required to wear protective clothing, which includes hard hats, gloves, safety glasses, coveralls (as an option) and steel-toed safety shoes. Workers required to climb (e.g., ladders, drilling masts) must be required to wear harnesses and lanyards and be tied off throughout the process.

For sampling operations that require drilling, open boreholes and wells must be covered or secured when unattended, including during crew breaks.

ELECTRICAL HAZARDS

Electric power often is supplied by gasoline or diesel engine generators. Working conditions may be wet, and electrical shock with possibly fatal consequences may occur. In addition, it is possible that drilling operations may encounter overhead or buried electrical utilities, potentially resulting in exposure to very high voltages, which could be fatal or initiate fires.

All electrical systems used during field operations should be checked for proper grounding during the initial installation. Temporary electrical power provided to the drill site shall be protected by ground fault circuit interrupters.

NOISE HAZARDS

Power equipment is capable of producing sound levels in excess of 85dB(A), the eight-hour threshold limit value recommended by the American Conference of Governmental Industrial Hygienists (ACGIH). Exposure to noise levels in excess of 85dB(A) for long periods of time can cause irreversible hearing loss. If noise levels exceed 85dB(A), a controlled area must be maintained at this distance with a posting at each entrance to the controlled area to read:

CAUTION NOISE HAZARD Hearing Protection Required Beyond This Point

HEAT STRESS

The use of protective clothing during summer months significantly increases the potential for personnel to experience heat stress. Adverse effects from heat stress include heat cramps, dehydration, skin rash, heat edema, heat exhaustion, heat stroke or death. When heat stress conditions exist, the following ought to be available:

- A cool and shaded rest area;
- Regular rest breaks;
- An adequate supply of drinking water; and
- Cotton coveralls rather than impermeable Tyvek coveralls.

CHEMICAL AND RADIOLOGICAL HAZARDS

The health and safety plan should contain information about a site's potential radionuclides and hazards that might be encountered during implementation of field sampling and survey procedures. All field personnel should read the health and safety plan and acknowledge an understanding of the radiological hazards associated with a site. Site specific training must be provided that addresses the chemical and radiological hazards likely to be associated with a site. Field procedures should include either information relating to these hazards or should reference appropriate sections of the Health and Safety Plan. References related to the use of protective clothing are given in EPA (1987), DOE (1987, Appendix J), and in 29 CFR 1910, Subpart I.

When procuring environmental solid and liquid samples, unusual characteristics such as color, suspended material, or number of phases and unusual odors should be noted and a description should be provided to the on-site safety officer as well as the analytical laboratory. Additional information concerning field methods for rapid screening of hazardous materials is presented in EPA (1987). This source primarily addresses the appearance and presence of organic compounds that might be present on occasions when one is collecting materials to detect radioactivity. Checking samples for chemical or radiological hazards can be as simple as visual inspection or using a hand-held radiation meter to detect radiation levels. Adjustments to laboratory procedures, particularly those involving sample handling and preparation, can only be made when pertinent field information is recorded and relayed to the project planner and to the laboratory. In some cases, a laboratory might not have clearance to receive certain types of samples (such as explosives or chemical agents) because of their content, and it will be necessary to divert these samples to an alternate laboratory. It might be necessary to reduce the volume sampled in order to meet shipping regulations if high concentrations of radioactivity are present in the samples. In some cases, the activity of one radionuclide might be much higher than others in the same sample. Adjustments made on the basis of the radionuclide of higher activity might result in collection of too little of another radionuclide to provide adequate detection and thus prevent identification of these radionuclides because of their relatively low minimum detectable

concentrations. These situations should be considered during planning and documented in the appropriate sampling plan document.

10.2.11.2 Biohazards

Precautions should be taken when handling unknown samples in the field. Some examples are wearing gloves, coveralls or disposable garments, plastic booties, dust masks or other respiratory protection. Some biohazards may be snakes, ticks, spiders, and rodents (Hanta virus). Prevention of potential exposure is the goal of a safety program. The type of protective equipment in the field should be discussed in the planning process and specified in the appropriate plan document. Since there are many specifics that are site dependent, it is difficult to create a comprehensive list. But the information is discussed to provide an awareness and starting point for additional discussion.

PERSONNEL TRAINING AND QUALIFICATION

All field operations that could lead to injury for sample collectors should be performed by personnel trained to documented procedures. When sampling is conducted in radiologically controlled areas (RCAs) as defined in regulatory standards (i.e., 10 CFR 20, 10 CFR 835). Formal training and qualification of field personnel may be required.

Training may require both classroom and practical applications in order to familiarize personnel with the basic theory of radiation and radioactivity and the basic rules for minimizing external exposures through time, distance, shielding, and avoidance of internal exposure (by complying with rules regarding smoking, drinking, eating, and washing of hands). Other topics to cover include common routes of exposure (e.g., inhalation, ingestion, skin contact); proper use of equipment and the safe handling of samples; proper use of safety equipment such as protective clothing, respirators, portable shielding, etc.

Guidance for the training and qualification of workers handling radioactive material has been issued by the Nuclear Regulatory Commission (see appropriate NRC NUREGs and Regulatory Guides on training of radiation workers), Department of Energy (1994), and the Institute of Nuclear Power Operations (INPO 88-010). These and other documents should be consulted for the purpose of training and qualifying field personnel.

PERSONNEL MONITORING AND BIOASSAY SAMPLING

When conditions dictate the need for personnel monitoring, various methods are commonly employed to assess external and internal exposure that might have resulted from the inhalation or ingestion of a radionuclide.

To monitor for external exposures to the whole body or extremities, thermoluminescent dosimeters (TLDs) or film badges may be used to document a worker's exposure. For internal exposures, assessment of dose may be based on: (1) air monitoring of the work area or the worker's breathing zone; (2) *in vivo* bioassay (whole-body counting); or (3) *in vitro* bioassays that normally involve urinalysis but may also include fecal analysis and nasal smears. For *in vitro* bioassays (i.e., urine or fecal), the standard method involves a 24-hour sample collection in a sealable container. Samples may be kept under refrigeration until laboratory analysis can be performed to retard bacterial action. (Bioassay sample collection is normally not performed in the "field.")

The following guidance documents may be used for personnel monitoring and the collection and preservation of bioassay samples:

- ANSI/ANS HPS N13.30 (1996), Performance Criteria for Radiobioassay;
- ANSI/ANS HPS N13.14 (1994), Internal Dosimetry Programs for Tritium Exposure—Minimum Requirements;
- ANSI/ANS HPS 13.22 (1995), Bioassay Programs for Uranium;
- ANSI/ANS HPS 13.42 (1997), Internal Dosimetry for Mixed Fission Activation Products;
- DOE Implementation Guide, Internal Dosimetry Program, G-10 CFR 835/C1—Rev. 1 Dec. 1994a;
- DOE Implementation Guide, External Dosimetry Program, G-10 CFR 835/C2—Rev. 1 Dec. 1994b;
- DOE Implementation Guide, Workplace Air Monitoring, G-10 CFR 835/E2-Rev. 1 Dec. 1994c;
- DOE Radiological Control Manual, DOE/EH-0256T, Rev. 1, 1994d;
- NRC Regulatory Guide 8.9, Acceptable Concepts, Models, Equations, and Assumptions for a Bioassay Program;
- NRC Regulatory Guide 8.11, Applications of Bioassay for Uranium;
- NRC Regulatory Guide 8.20, Applications of Bioassay for ^{125}I and ^{131}I;
- NRC Regulatory Guide 8.22, Bioassays at Uranium Mills;
- NRC Regulatory Guide 8.26, Applications of Bioassay for Fission and Activation Products;
- NRC Regulatory Guide 8.32, Criteria for Establishing a Tritium Bioassay Program;
- NCRP (1987), Use of Bioassay Procedures for Assessment of Internal Radionuclides Deposition; and
- INPO (1988), Guidelines for Radiological Protection at Nuclear Power Stations.

Part II: Matrix-Specific Issues That Impact Field Sample Collection, Processing, and Preservation

Field processing should be planned in advance so that all necessary materials are available during field work. Preparing checklists of processing equipment, instruments, and expendable materials—as exemplified in part by lists accompanying sampling procedures described by EPA

1994—helps this planning effort and serves to organize field methods. Field personnel who communicate problems should prevent loss of time, effort, and improper sample collection, as well as documents exactly what equipment, instruments, etc. were used.

The initial steps taken in the field frequently are critical to the laboratory analysis performed hours, days, or even weeks after a sample is obtained. Various sample preparation steps may be required before samples are packaged and shipped for laboratory analysis. The need for sample processing and preservation is commonly determined by the sample matrix, the data quality objectives of the analysis, the nature of the radionuclide, and the analytical method.

The goal of sample preservation is to maintain the integrity of the sample between the time the sample is collected and the time it is analyzed, thus assuring that the analysis is performed on a sample representative of the media collected. In general, the aim of sample preservation is to limit biological and chemical actions that might alter the concentration or physical state of the radionuclide constituents or analytes. For example, cations at very low concentrations can be lost from solution (e.g., cesium can exchange with potassium in the glass container, and radionuclides can be absorbed by algae or slime growths in sample lines or containers that remain in the field for extended periods). Requirements for sample preservation should be determined during project planning when analytical protocols are selected. Sample preservation in the field typically follows or accompanies processing activities.

This section provides matrix-specific guidance that focuses on the preparation and processing of field samples. In order to assist project planners in developing a sampling plan, a limited discussion is also provided that describes matrix-specific methods commonly employed for the collection of field samples. Guidance is presented for only the most common materials or environmental media, which are generically classified as liquids, solids, and air. In some instances, a solid material to be analyzed involves particulate matter suspended in a liquid or air that is commonly obtained by filtration. Because filter media can affect analytical protocols, a separate discussion is provided that addresses sample materials contained on filter materials, including surface contamination associated with wipe samples.

10.3 Liquid Samples

Liquid samples are typically classified as aqueous, non-aqueous, and as mixtures. Aqueous samples requiring analysis are likely to represent surface water, ground water, drinking water, precipitation, tanks and lagoons, and runoff. Non-aqueous liquids may include a variety of solvents, oils and other organic liquids. Mixtures of liquids represent a combination of aqueous and non-aqueous liquids or a solid suspended in either aqueous and non-aqueous liquids. Standardized water sampling procedures are described in numerous documents (APHA, 1996; EPA, 1985; EPA, 1987; DOE, 1997; ASTM D3370). Important decisions include the choice of instrument or tool used to obtain the sample, the sample container material, the need for sample filtration, and the use of sample preservatives.

10.3.1 Liquid Sampling Methods

The effect of the sample collection process on the sample integrity needs to be understood and managed. Two examples are dissolved gases and cross contamination. It may be necessary to minimize dissolved oxygen and carbon dioxide which may cause some dissolved metals to undergo reaction or precipitation.

Sampling is discussed in Navy Environmental Compliance Sampling and Field Testing Procedures Manual, NAVSEA T0300-AZ-PRO-010. USACE discusses sampling in *Technical Project Planning Guidance for Hazardous, Toxic and Radioactive Waste (HTRW) Data Quality Design, Engineer Manual* EM-200-1-2, Appendix H, Sampling Methods, July 1995. This reference has been superseded but the revision does not include sampling. The sampling references listed in Appendix H are:

- U.S. Environmental Protection Agency (EPA). 1984. Characterization of Hazardous Waste Sites—A Method Manual, Vol. II, Available Sampling Methods, Second Edition, EPA 600-4-84-076.

- U.S. Environmental Protection Agency (EPA). 1982. Handbook for Sampling and Sample Preservation of Water and Wastewater, EPA 600-4-82-029.

- U.S. Environmental Protection Agency (EPA). 1986. Compendium of Methods for Determination of Superfund Field Operation Methods, EPA 600-4-87/006.

- U.S. Environmental Protection Agency (EPA). 1987. A Compendium of Methods for Determination of Superfund Field Operation Methods, EPA 540-P-87-001a, OSWER Directive 9355.0-14.

- U.S. Department of the Interior. 1980. National Handbook of Recommended Methods for Water for Water-Data Acquisition, Volume I and II.

10.3.2 Liquid Sample Preparation: Filtration

Filtration of a water sample may be a key analytical planning issue and is discussed in Chapter 3, Section 3.3.2. A decision needs to be made during project planning whether or not to filter the sample in the field. Filtration of water or other liquids may be required to determine contaminant concentrations in solubilized form, suspended particulates, or sediment. The method of filtration will depend on the required sample volume, the amount and size of suspended particulates, and the availability of portable equipment and resources (e.g., electricity).

The potential need to filter a water sample principally depends on the source of water and the objectives of the project investigation. If, for example, the source of water is drinking water "at-

the-spigot" and the intent is to assess human internal exposure from ingestion, unfiltered tap water samples are likely to be required. Conversely, filtration may be required for water taken from an unlined field monitor well that is likely to contain significant amounts of particulate matter. These solids are of little relevance but may interfere with radioanalytical protocols (e.g., sample absorption may occur during gross alpha or beta counting where the analytical procedure involve s the simple evaporation of a water aliquant on a planchet).

For remote sampling sites, sample processing may be restricted to gravity filtration that requires a minimum of equipment and resources. Drawing samples through filters by pressure or suction that is created by syringe, vacuum pump, or aspiration are alternative options. If filter papers or membranes capture materials that will be retained for analysis, they should be handled with clean rubber or plastic gloves, forceps, or other instruments to prevent sample contamination.

Each Federal Agency may have unique guidance to determine the need and process for filtering samples. One performance-based example is that of EPA, discussed in the next section. This guidance applies to either the field or laboratory filtration.

10.3.2.1 EPA Guidance for Samples/Filtration

The Special Topics Subcommittee of EPA's Science Advisory Board's Environmental Engineering Committee met to examine the question of whether or not to filter ground-water samples when analyzing for metals in the context of a review of the Office of Emergency and Remedial Response's (OERR) proposed guidance on field filtration of ground-water samples taken from monitoring wells for metals analysis as part of a Superfund site assessment (EPA, 1997). The key findings of the Subcommittee were:

- Several factors could introduce errors in the sampling and analysis of ground water for metals or metallic radionuclides. Well construction, development, sampling, and field filtering are among the steps that could influence the metals measured in the ground-water samples. Field filtering is often a smaller source of variability and bias compared to these other factors. Therefore, the Agency should emphasize in its guidance the importance of proper well construction, development, purging, and water pumping rates so that the field filtering decisions can also be made accurately.

- Under ideal conditions, field-filtered ground-water samples should yield identical metals concentrations when compared to unfiltered samples. However, under non-ideal conditions, the sampling process may introduce geological materials into the sample and would require field filtration. Under such conditions, filtering to remove the geological artifacts has the potential of removing colloids (small particles that may have migrated as suspended materials that are mobile in the aquifer). Available scientific evidence indicates that when wells have been properly constructed, developed, and purged, and when the sample has been collected without stirring or agitating the aquifer materials (turbidity less than 5 nephelometric turbidy

units, NTU), then field filtering should not be necessary. For Superfund site assessments, the low-flow sampling technique without filtration is the preferred sampling approach for subsequent metal analysis when well construction, well maintenance, and hydrogeological conditions such as flow rate allow. Under such conditions, the collected samples should be representative of the dissolved and particulate metals that are mobile in ground-water systems. The Agency's proposal to rely on low flow sampling and unfiltered samples is a conservative approach that favors false positives over false negatives.

- When the turbidity of the sample is high, the situation is different. In-line filtering provides samples that retain their chemical integrity. Therefore, field filtering of properly collected ground-water samples should be done when turbidity in the samples is higher than 5 NTU, even after slow pumping has been utilized to obtain the sample.

They acknowledged, however, that differences in the way wells are installed, their packing materials, and the techniques used to collect ground-water samples can lead to variability in analytical results between wells and between individual samples. Filtering a sample can be seen as a way to remove suspended particles and some colloids that contain metals that would not normally be in the ground water if the material were not disturbed during sampling. Here a colloid is defined as a particle that ranges in size from 0.003 to 10 µm (Puls et al., 1990) or particles having diameters of less than 10µm (Puls and Powell, 1992). The literature indicates that colloids as large as 2 µm can be mobile in porous media (Puls and Powell., 1992), and that colloid concentration can be as high as 1,000 times higher in fractured granitic systems (McCarthy and Deguelde, 1993). Saar (1997) presents a review of the industry practice of filtration of ground-water samples. For some sites with low hydraulic conductivity the presence of an excess of colloids presents numerous monitoring challenges and field filtration might be necessary.

The desire to disturb the aquifer as little as possible has led to the use of low-flow sampling of wells—low-flow purging and sampling occurs typically at 0.1 to 0.3 L/min (Saar, 1997). The low-flow technique maximizes representativeness by (EPA, 1997):

- Minimizing disturbances that might suspend geochemical materials that are not usually mobile;

- Minimizing disturbances that might expose new reactive sites that could result in leaching or adsorption of inorganic constituents of ground water;

- Minimizing exposure of the ground water to the atmosphere or negative pressures, ensuring that the rate of purging and sampling does not remove ground water from the well at a rate much greater than the natural ground-water influx; and

- Monitoring indicator parameters to identify when stagnant waters have been purged and the optimum time for sample collection.

In summary, based on the ability of the low-flow sampling technique to collect representative samples, EPA suggests that filtering of ground-water samples prior to metals analysis is usually not required (EPA, 1997).

10.3.2.2 Filters

When filtration is required, it should be done in the field or as soon as practicable. The advantages of filtering in the field are that acid preservatives can be added shortly thereafter which minimizes both the adsorption of soluble contaminants and avoids the dissolution of particulate matter, volume reduction, and waste reduction. Unless specific requirements dictate otherwise, the removal of suspended particles is commonly achieved by filtration that removes particles larger than 0.45 µm (ASTM D3977).

In other instances, the investigative objectives may not be restricted to water-solubilized contaminants but include analysis of contaminated suspended particulate matter. To detect the presence of radionuclides that are highly insoluble, such as isotopes of uranium, thorium, and plutonium, analysis of particulate matter is considered more sensitive than the filtered water (EPA, 1994).

The fact that small particles pass through membrane filters has been recognized for some time (Kennedy et al., 1974). The arbitrary cutoff of 0.45 µm between dissolved and suspended matter has gained such wide use that it is the filter size that is commonly recommended by laboratory protocols. Filtering through a 0.45 µm filter may take considerable time and may require suction or pressure to accomplish in a reasonable time.

It should be noted, however, that manufacturers of filters usually specify only what will not pass through the filter; they make no claims concerning what actually does pass through the filter. Laxen and Chandler (1982) present a comprehensive discussion of some effects of different filter types. They refer to thin (5 to 10 µm) polycarbonate filters as screen types, and thick (100 to 150 µm) cellulose nitrate and acetate filters as depth types. The polycarbonate-screen type clogs much more rapidly. Once the filtration rate drops, particles that would normally pass through the filter are trapped in the material already retained. Hence, the use of so-called polycarbonate-screen filters, because of their increased propensity to clog, is generally not recommended.

In addition to the difficulty of contending with clogging, Silva and Yee (1982) report adsorption of dissolved radionuclides on membrane filters. Although these drawbacks cannot be completely overcome, they are still less than the potential difficulties that arise from not filtering.

Finally, good laboratory practices must be used for field sampling. The most likely sources of contamination for the filters are improperly cleaned tubing and filter holders and handling the filters with contaminated fingers. Tubing and holders should be thoroughly cleaned and rinsed between samples and the entire system should be rinsed several times with the water to be sampled. Filters should be handled with clean rubber gloves.

10.3.3 Field Preservation of Liquid Samples

Sample degradation may occur between the time of collection and analysis due to microbial contaminants or chemical interactions. Although sample degradation cannot destroy or alter the radiological properties of a contaminant, it can alter the radionuclide's chemical properties and its potential distribution within a sample. For example, microbial processes are known to affect both the chemical state and the distribution of radioelements due to oxidation-reduction reactions, complexation and solubilization by metabolic compounds, bioaccumulation, biomylation, and production of gaseous substances such as CO_2, H_2, CH_4, and H_2S (Francis, 1985; Pignolet et al., 1989).

10.3.3.1 Sample Acidification

Acidification is the method of choice for preserving most types of water samples. The principal benefit of acidification is that it keeps many radionuclides in solution and minimizes their potential for removal by chemical and physical adsorption or by ion exchange. The mode by which a radionuclide is potentially removed from solution is strongly affected by the radionuclide and the container material. For example, studies conducted by Bernabee et al. (1980) and Milkey (1954) demonstrated that the removal of metal ions from solution is dominated by physical (i.e., van der waals) adsorption. Their conclusion is based on: (1) their observation that the loss of uranium, lead, and thorium ions from solution was significantly greater for containers made of polyethylene when compared to borosilicate glass; and (2) the fact that while adsorption by glass may potentially involve all three adsorption processes; with polyethylene plastic, there are no valence-type attractive forces or ions to exchange and only physical van der waals adsorption is possible.

Similar observations were reported by: (1) Dyck (1968), who compared long-term adsorption of silver ions by molded plastic to glass containers; (2) Jackson (1962), who showed that polyethylene containers absorbed about five times as much ^{90}Sr as glass containers at pH of about seven; and (3) Martin and Hylko (1987a; 1987b), who reported that greater than 50 percent of ^{99}Tc was adsorbed by polyethylene containers from non-acidified samples.

For sample acidification, either nitric or hydrochloric acid is commonly added until a pH of less than two. Table 7010:1 in *Standard Methods for the Examination of Water and Wastewater* (APHA, 1995) and Method 900.0 in *Prescribed Procedures for Measurement of Radioactivity in*

Drinking Water (EPA, 1980) provide additional guidance. Guidance for sample preservation by acidification has been issued by Federal Agencies and others as summarized below.

In instances of very low activity samples where container adsorption poses a significant concern, but where acidification of the sample interferes with the radioanalytical method, the choice of sample container may be limited to glass or require alternative methods. For example, the use of acids as a preservative is not recommended for the analysis of tritium (^{3}H), carbon-14 (^{14}C), or radon in water, and precautions must be taken for the following reasons:

- For radon, sample preservation offers no benefit and is therefore not required for analytical accuracy.

- The addition of acid to a sample containing ^{14}C may result in the production of $^{14}CO_2$ and the loss of radioactivity from the sample.

- The adverse impact of acid on tritiated water is due to the fact that water dissociates and recombines continuously (i.e., $H_2O \_ H^+ + OH^-$ or $HO \_ T^+ + OH^-$). The tritium ion that was part of the water molecule may, therefore, be exchanged for the hydrogen ion from the acid. The impact of this exchange is realized as a result of distillation, which is a common method for purifying water in preparation for liquid scintillation counting. When the sample is heated and the distillate is collected on a cold finger, distilled tritiated water, in the presence of acid, would have a reduced specific activity over the original sample.

Although acidification has been shown to effectively reduce the adsorption of technetium by polyethylene, technetium in the TcO_4^{-4} state has been observed to volatilize in strong acid solutions during evaporation while preparing water samples for gross beta analysis (NAS, 1960). To hasten evaporation, the planchet is commonly flamed. This dilemma can be resolved by either precoating planchets with a film of detergent prior to the addition of the acidified water sample or by passive evaporation of the acidified water sample that avoids the higher temperature associated with flaming (Blanchard et al., 1993).

10.3.3.2 Non-Acid Preservation Techniques

If a sample contains significant organics, or if contaminants under investigation react with acids that interfere with the radioanalytical methods, other methods of sample preparation should be considered.

REFRIGERATION AND FREEZING

The effect of refrigeration or freezing temperatures to arrest microbial activity is a fundamental concept. Temperatures near the freezing mark or below not only retard or block bacterial growth but arrest essentially all other metabolic activity. It should, however, be noted that most bacteria

748 can survive even in extreme temperatures. (Indeed, if a suspension of bacterial cells is frozen
749 rapidly with no appreciable formation of ice crystals, it can be kept at temperatures as low as
750 -194° C for indefinite periods of time with little loss of viability.)

751 The choice between refrigeration and freezing is dictated by the potential impacts of ice
752 formation on sample constituents. Besides physical changes of organic constituents, the initial
753 formation of ice crystals and the exclusion of any solutes may concentrate the solutes to the point
754 of precipitation. Quick freezing methods that minimize ice crystal formation are beneficial for
755 preserving some organic constituents. Quick freezing is commonly done by packing sealed
756 samples in liquid nitrogen or dry ice. Care must be taken, however, to avoid container breakage
757 due to sample volume expansion. An air space of a least 10 percent and a container made of
758 plastic provide reasonable assurance for container integrity.

759 When refrigeration is employed, attempts should be made to avoid temperatures that could result
760 in slow freezing and the formation of ice crystals. Optimum refrigeration temperatures for sample
761 preservation at 4 ± 2° C can be achieved by packing samples in ice or freeze packs within a
762 thermally insulated leak-proof container (ASTM D3856; ASTM D3370).

763 PAPER PULP

764 Adsorption and loss of radionuclides over time to the container wall can be avoided with the
765 addition of paper pulp. Due to its adsorptive property and large surface, paper pulp has been
766 shown to remove more than 95 percent of radionuclides from solution (Bernabee et al., 1980).
767 About two grams of finely ground paper pulp are added per liter of acidified sample at time of
768 collection. The pH should be adjusted to one or less and vigorously shaken. The sample may be
769 stored in this condition for an extended period of time. To prepare for analysis, the pulp is
770 removed from solution by filtration and subjected to wet ashing using strong acids (Chapter 12).
771 This ashed solution is commonly added to the original filtrate to make a reconstituted sample
772 solution.
773
774 The use of paper pulp and the need for wet ashing, however, pose problems for certain
775 radioanalytical laboratory protocols and must therefore be thoroughly evaluated.

776 SULFITE

777 To prevent the loss of radioiodine from solution, sodium bisulfite ($NaHSO_3$) or sodium
778 metabisulfite ($Na_2S_2O_5$) may be used. These compounds act as strong reducing agents and
779 prevent the volatilization of iodine. If acid is also employed to preserve samples for analysis of
780 other radionuclides, it is important to note that acid will negate the reductant's effectiveness in
781 behalf of iodine. For this reason, samples collected for iodine analyses typically are collected and
782 preserved in a separate container. It should also be noted that the reducing environment produced
783 by the sulfite preservative may render iron, uranium, and other easily reduced elements or their

compounds to an insoluble state. The loss of reduced insoluble radionuclides from solution will have an obvious adverse impact on radioanalytic measurements that require chemical separation. Chapter 14.9 has additional information on carriers and tracers.

OTHERS

Other methods that have been used to preserve liquid samples containing organics and biological materials include chemical preservatives (e.g., formaldehyde and methanol) or quick freezing by means of liquid nitrogen. Table 10.1 summarizes the advantages and disadvantages of these and previously described preservation methods.

TABLE 10.1—Summary of sample preservation techniques.

Preservation Technique	Advantages	Disadvantages
Addition of HNO_3	Reduces pH and inhibits plating of metals on container walls.	Strong oxidizer that might react with organic compounds. Tritium might be separated preferentially as acid hydrogen; ^{14}C might be lost as $^{14}CO_2$.
Addition of Hcl	Reduces pH and inhibits plating of metals on container walls. Chloride forms strong anionic complexes with Iron and Uranium.	Tritium will be preferentially separated as acid hydrogen; ^{14}C might be lost as $^{14}CO_2$. Might cause corrosion of stainless steel planchets on gross analyses.
Addition of Sulfite	Forms a reducing environment to prevent the volatilization of iodine.	Might produce insoluble compounds from reduced forms of iron or uranium.
Addition of Formaldehyde	Preserves organic samples. Prevents further biological activity.	May create disposal problems.
Cooling (Ice at approximately 0° C)	Preserves organic samples (i.e., water, foods). Reduces dehydration and retains moisture. Reduces biological activity.	Ice melts, requiring replacement over time.
Freezing (Dry Ice at approximately -78° C)	Preserves organic samples (i.e., water, plant, animal). Suspends biological activity.	Dry ice sublimates and requires replacement.
Addition of Paper Pulp	Provides large surface area for adsorption of metals, thus minimizing adsorption on container walls.	Requires pH to be one or less. Requires filtration and wet ashing of paper pulp and combining liquids to make a new solution.

10.3.4 Liquid Samples: Special Cases

In some cases, liquid samples require special handling in order to preserve or retain a volatile or gaseous radionuclide. The following are examples of specific methods used to recover or preserve such samples of interest.

10.3.4.1 Radon-222 in Water

Waterborne radon is analyzed most commonly by liquid scintillation methods, although gamma spectroscopy and other methods have been employed or proposed. Liquid scintillation has the obvious advantage of being designed for automated sample processing and is, therefore, less labor intensive or costly. A key to consistency in analytical results is the zero headspace sampling protocol such as the one described below.

Since radon is inert and nonpolar, it diffuses through plastic more rapidly than glass. The use of plastic scintillation vials, therefore, leads to significant loss of radon in water (Whittaker, 1989; Hess and Beasley, 1990). For this reason, it is recommended that the water sample is collected in a 23 mL glass scintillation vial, capped with a Teflon or foil-lined cap.

Samples are collected from a non-aerated faucet or spigot, which has been allowed to flow for sufficient time so that the sample is representative of the water in the distribution system or well. The time will vary depending on the source. The following zero headspace procedure will minimize the loss of radon from the sample during collection:

- Place sample vial in a 300-600 mL beaker or other suitable container and attach the universal adapter and fill-line to spigot, and start the flow.
- Fill the vial to prevent it from floating. Then fill the beaker until the vial is submerged.
- Place the tip of the fill line about two thirds of the way into the vial and fill until approximately two or more vial (50-100 mL) volumes have been displaced.
- Carefully remove the vial with a pair of 10-inch tweezers and cap the vial with a Teflon or foil-lined cap. Invert the sample and check for air bubbles. If any bubbles are present, discard the sample and repeat the sampling procedure. Record date and time the sample was collected and store the sample in a cooler to prevent temperature excursions. Transport the samples to the laboratory in a cooler or other suitable insulated package.

10.3.4.1 Milk

Milk commonly is viewed as the food product of greatest potential dose significance for airborne releases of radionuclides. Due to the metabolic discrimination, however, only a few radionuclides

have a significant dose impact via the milk pathway, notably ^{90}Sr, ^{131}I, and ^{137}Cs. Raw milk should be obtained from the closest cows or goats downwind from a source.

To prevent milk from souring or curdling, samples should be refrigerated. Preservation of milk may also be achieved through the addition of formaldehyde or methanol (DOE, 1987), merthiolate, or Thimerosal (EPA, 1994). Analytical procedures for select radionuclides in milk are well established and should be considered when deciding on a sample preservation method.

Owing to the volatility and potential loss of ^{131}I, a known amount of NaI dissolved in water should be added to the milk sample at time of collection. The NaI not only serves as a carrier for the chemical separation of radioiodine, but also provides a quantitative tool for determining any loss prior to analysis (DOE, 1990).

10.3.5 Non-aqueous Liquids and Mixtures

Non-aqueous liquids and mixtures include a wide range of organic fluids or solvents, organic materials dissolved in water, oils, lubricants, etc. These liquids are not likely to represent contaminated environmental media or matrices, but most likely represent waste streams that must be sampled. Non-aqueous waste streams are generated as part of normal operations by nuclear utilities, medical facilities, academic and research facilities, State and Federal Agencies, radio-pharmaceutical manufacturers, DOE weapons complexes, mining and fuel fabrication facilities, etc. Examples of these non-aqueous liquids and mixtures include waste oils and other lubricants that are generated routinely from maintenance of various types equipment associated with nuclear power plant operations or the production of nuclear fuel and nuclear weapon components; and organic and inorganic solvents, acids, and bases that are used in a variety of medical, research, and industrial applications.

In addition to the production of non-aqueous liquid wastes from routine operations by these facilities, large quantities of non-aqueous liquids containing radionuclide contaminants are also generated by routine facility decontamination efforts and final decontamination associated with facility decommissioning. For decontamination and decommissioning activities, a wide range of processes have been developed that employ halogenated organic compounds, such as Freon, chloroform, or trichloroethane. Other aggressive chemical decontamination processes involve dissolution and removal of metal and oxide layers from surfaces using acid solutions (e.g., sulfuric acid, nitric acid, phosphoric acids, and oxalic acid). Chemical decontamination also may use chelating agents in concentrated processes (5 to 25 percent wt. chemical in solution) and dilute processes (one percent wt. or less chemicals in solution). Examples of chemical processes that can be used in both concentrated and dilute forms include the low oxidation-state transition-metal ion (LOMI) and LOMI-nitric permanganate, developed by Dow Chemical Company and AP/Citron. The reagents used in both the concentrated and dilute processes include chelating and complexing agents such as ethylene diamine tetra acetic acid (EDTA), diethylene triamine penta-acetic acid (DTPA), citric acid, oxalic acid, picolinic acid, and formic acid. Chelating agents and

organic acids are used in decontamination formulas because they form strong complexes with actinides, lanthanides, heavy metals, and transition metals and assist in keeping these elements in solution.

Generally, these chemical decontamination solutions, once used, are treated with ion-exchange resins to extract the soluble activity. The ion-exchange decontamination solutions must, nevertheless, be sampled to assess the amount of residual radioactivity.

The radionuclides that may be encountered with non-aqueous liquids and mixtures depend on both the nature of the liquid and its usage. The following listing of radionuclides and liquids are based on published data collected by NRC (1992) and the State of Illinois (Klebe 1998; IDNS 1993-1997):

- Toluene/xylene/scintillation fluids used by research and clinical institutions: ^{3}H, ^{14}C, ^{32}P, ^{35}S, ^{45}Ca, ^{63}Ni, ^{99}Tc, ^{90}Sr, ^{125}I, ^{147}Pm, $^{226/228}Ra$, $^{228/230/232}Th$, $^{234/235/238}U$, $^{238/239/241}Pu$, ^{241}Am.

- Waste oils and lubricants from operation of motors, pumps, and other equipment: ^{3}H, ^{54}Mn, ^{65}Zn, ^{60}Co, $^{134/137}Cs$, $^{228/230/232}Th$.

- Halogenated organic and solvents from refrigeration, degreasing, and decontamination: ^{3}H, ^{14}C, ^{32}P, ^{35}S, ^{54}Mn, $^{58/60}Co$, ^{63}Ni, ^{90}Sr, $^{125/129}I$, $^{134/137}Cs$, $^{226/228}Ra$, $^{228/230/232}Th$, $^{232/234/238}U$, $^{238/239/241}Pu$, U-nat.

- Other organic solvents from laboratory and industrial operations and cleaning: ^{3}H, ^{32}P, ^{35}S, ^{45}Ca, ^{125}I, U-nat.

- Inorganic and organic acids and bases from extraction processes and decontamination: ^{3}H, ^{14}C, ^{32}P, ^{35}S, ^{54}Mn, ^{67}Ga, ^{125}I, ^{60}Co, ^{137}Cs, $^{201/202}Th$, and U-nat.

Due to the large number of potential non-aqueous liquids and the complex mixtures of radionuclide contaminants that may require radiochemical analysis, a comprehensive discussion of sample preparation and preservation is beyond the scope of this discussion. In most instances, however, these samples are not likely to require refrigeration or chemical preservatives that protect against sample degradation.

Some organic solvents and highly acidic or basic liquids may react with plastic containers, causing brittleness or breakage. In selecting sample containers for these non-aqueous samples, it is important to assess the manufacturers product specifications, which typically provide information regarding the container's resistance to chemical and physical agents. When non-aqueous samples are stored for long periods of time, containers should be checked routinely.

10.4 Solids

907
908 Solid samples consist of a wide variety of materials that include soil and sediment, plant and
909 animal tissue, metal, concrete, asphalt, trash, etc. In general, most solid samples do not require
910 preservation, but require specific processing in the field before transporting to the laboratory for
911 analysis. For example, soil sample field processing may require sieving in order to establish
912 sample homogeneity. These and other specific handling requirements are described below in the
913 section on each type of solid sample.

914 The most critical aspect is the collection of a sufficient amount of a representative sample. One
915 purpose of soil processing is to bring back only that sample needed for the laboratory. Unless
916 instructed otherwise, samples received by the laboratory are typically analyzed exactly as they are
917 received. This means that extraneous material should be removed at the time of sample
918 collection, if indicated in the appropriated plan document.

919 In many instances, sample moisture content at the time of collection is an important factor. Thus,
920 the weights of solid samples should be recorded at the time a sample is collected. This allows one
921 to track changes in wet weight from field to laboratory. Dry and ash weights generally are
922 determined at the laboratory.

923 Unlike liquid samples that may be introduced or removed from a container by simple pouring,
924 solid samples may require a container that is designed for easy sample placement and removal.
925 For this reason, large-mouth plastic containers with screw caps or individual boxes with sealable
926 plastic liners are commonly used. The containers also minimize the risk for breakage and sample
927 cross-contamination.

928 **10.4.1 Soils**
929
930 ASTM D653 (*Standard Terminology Relating to Soil, Rock, and Contained Fluids*) defines soil
931 as: "Sediments or other unconsolidated accumulations of solid particles produced by the physical
932 and chemical degradation of rocks, and that might or might not contain organic matter." ASTM
933 C999 provides generic guidance for soil sample preparation for the determination of
934 radionuclides. The American Society for Testing and Materials provides additional information
935 on soil and rock in the following standards:

936 • ASTM D 4914, Section 4, Construction, Volume 4.08 Soil and Rock (I).
937 • ASTM D 4943, Section 4, Construction, Volume 4.09 Soil and Rock (II): Geosynthetics.

938 The distribution of radionuclides in soil should be assumed to be heterogeneous. The degree of
939 heterogeneity is dictated by the radionuclide's mode of entry into the environment and soil, the
940 chemical characteristics of the radionuclide contaminant, soil composition, meteorological and
941 environmental conditions, and land use. For example, soil contamination from an airborne
942 release of a radionuclide with strong affinity for clay or other mineral constituents of soil (i.e.,

high k_d value) will likely exhibit a gradient with rapidly diminishing concentrations as a function of soil depth. Moreover, contamination may be differentially distributed among soil particles of different sizes. In most cases, because the contaminant is adsorbed at the surface of soil particles and since the surface-to-volume ratio favors smaller particles, smaller soil particles will exhibit a higher specific activity when compared to larger particles. If land areas include areas of farming, tilling of soil will clearly impact the distribution of surface contamination.

10.4.1.1 Soil Sample Preparation

Extraneous material should be removed at the time of sample collection, if indicated in the appropriate plan document. The material may have to be saved and analyzed separately, depending on the project requirements and MQOs. If rocks, debris, and roots are removed from a soil sample after it arrives at the laboratory, there might not be sufficient material to complete all the requested analyses. A sufficient amount of sample should be collected to provide the net quantity necessary for the analysis. Subsequent drying at the laboratory may remove a large percentage of the sample weight that is available for analysis. Field-portable balances or scales may be used to weigh samples as they are collected, further ensuring sufficient sample weights are obtained. For certain types of samples, the project DQOs may require maintaining the configuration of the sample, such as core samples where concentration verses depth will be analyzed.

The project plan should address the impact of heterogeneity of radionuclide distribution in soil. Some factors to consider that may impact radionuclide distribution are: determining sampling depth, the need for removal of vegetative matter, rocks, and debris, and the homogenation of soil particulates. For example, soil sampling depths of the top 5 cm is recommended for soils contaminated by recent airborne releases (ASTM C998); soil depth to 15 cm may be appropriate when exposure involves the need to monitor the root zone of food crops (MARSSIM, 2000; NRC, 1990). The need for sample field QC, such as field splitting, should be evaluated. Some types of field QC can be used to evaluate the extent of radionuclide homogeneity. In general, no special preservation measures are required for soil samples; however, preliminary soil sample preparation involving drying, sieving, homogenizing, and splitting may be performed by a field laboratory prior to sample shipment to the analytical laboratory.

If volatile elements are among other non-volatile contaminants, samples must be fractionated before drying to avoid loss of the contaminant of interest. Dried samples are homogenized by mortar and pestle, jaw crusher, ball mill, parallel plate grinder, blender, or a combination of these techniques and sieved to obtain a uniform sample. Sieve sizes from 35 to 200 mesh generally are recommended for wet chemistry procedures. ASTM C999 correlates various mesh sizes with alternative designations, inclusive of physical dimensions expressed in inches or in the metric system. In addition, samples for chemical separations are usually ashed in a muffle furnace to remove any remaining organic materials that may interfere with the procedures.

10.4.1.2 Sample Ashing

Soil samples that require chemical separation for radionuclide analysis may also be ashed by the field laboratory. The use of the term "field laboratory" can cause confusion, since no one definition is possible. It is used here to define a lab that is close to the point of sample collection. In no way does it imply that there is a distinction in requirements or specifications that impact quality. For soil samples, ashing is performed in a muffle furnace to remove any organic materials that may interfere with radiochemical procedures.

10.4.2 Sediments

Sediments of lakes, reservoirs, cooling ponds, settling basins, and flowing bodies of surface water may become contaminated as a result of direct liquid discharges, wet surface deposition, or from runoffs associated with contaminated soils. Because of various chemically and physically binding interactions with radionuclides, sediments serve as integrating media that are important to environmental monitoring. An understanding of the behavior of radionuclides in the aquatic environment is critical to designing a sampling plan, because their behavior dictates their distribution and sampling locations. Sediment cores may be sampled, frozen, and then sectioned.

The fate of radionuclides entering surface waters and their subsequent interaction with sediment is complex due to numerous mechanisms and processes that affect the initial mixing and dispersion of radionuclides, their distribution in water, sediment, plants and animals, and their long-term retention within these compartments. Several factors must be considered to establish appropriate sediment sampling locations and depths and are discussed briefly below.

10.4.2.1 Initial Mixing and Transport Dispersion of Radionuclides Discharged to Water

The rapid initial mixing phase in the nearfield is dominated by the characteristics of the effluent and the outfall structure. The extent of nearfield mixing and dilution is strongly affected by the quantity of effluent relative to the receiving body of water, the level of turbulence produced by means of the discharge momentum (jet action), the discharge buoyancy (plume action), the outfall configuration, and the depth and current flow rate in the vicinity of outfall.

Predictive models have been proposed for surface and submerged discharges; single point and multi-point outfalls; deep and shallow, stagnant and flowing water; and buoyant (positive and negative) and non-buoyant effects. An understanding of the basic hydrodynamic variables that define each of these conditions will aid in the selection of sampling locations.

In the case of small and medium bodies of surface waters, where vertical thermal stratification is the primary factor that determines inflow and outflow dynamics, a simple one- or two-dimensional model may be appropriate as discussed in Regulatory Guide 1.113 (NRC 1977). For large bodies of surface water where neither horizontal nor vertical homogeneity can be assumed,

more complex three-dimensional dispersion models must be applied to properly assess hydrodynamics and the distribution of radionuclides in sediment. A review of numerical hydrodynamic models for large bodies of surface waters has been presented by Johnson (1980).

10.4.2.2 Sediment Effect

Following initial mixing in the nearfield (i.e., outfall), subsequent transport and distribution of a dissolved radionuclide is greatly impacted if the radionuclide is absorbed strongly from solution onto sediments by processes that include ion exchange, precipitation-mineral formation, complexation-hydrolysis, and oxidation-reduction. Both suspended and less-mobile bed sediments may absorb radionuclides, but suspended sediments usually absorb more efficiently per unit weight than bed sediments (Friend et al., 1965; Parker et al., 1965).

The impacts of sediment absorption in a flowing body of water are obvious: the required time for sediment absorption allows the dissolved radionuclide to move considerable distances downstream before being absorbed, and sediment absorption steadily reduces the concentration of dissolved radionuclides with the result that an activity gradient is established in downstream water, sediment, and aquatic biota. Concentration gradients are further complicated by the high mobility of suspended sediments, the slow but steady erosion of bed sediments, the mobility and transfer of the radionuclide contaminant that has entered the aquatic food web, and the various mechanisms that modify sediment adsorption and desorption.

10.4.2.3 Sample Preparation/Preservation

In most cases, sediment is separated from water by simple decanting, but samples also may be obtained by filtering a slurry or through passive evaporation. As noted previously, care must be taken to avoid cross contamination from sampling by decontaminating or replacing tools and also from avoiding contact between successive samples. Suitable sample containers include glass or plastic jars with screw caps. The presence of volatile or semi-volatile organic and micro-organisms may impact the radionuclide concentration, therefore, samples should be kept on ice while in the field and refrigerated while awaiting radioanalysis.

10.4.3 Other Solids

10.4.3.1 Structural Materials

In some cases, a project plan requires sample analysis of structural materials such as concrete or steel. Concrete from floors, walls, sidewalks or road surfaces is typically collected by scabbling, coring, drilling, or chiseling. Depending on the radionuclides of interest and detection methods, these sample preparations may require crushing, pulverization, and sieving.

Metal associated with structures (e.g., I-beams, rebar) or machines may be contaminated on exterior or interior surfaces or through activation may become volumetrically contaminated. Surface contamination may be assessed by swipe samples that provide a measure of removable contamination (Section 10.7) or by scraping, sandblasting, or other abrasive techniques. Volumetric contamination is frequently assessed by non-destructive field measurements that rely on gamma-emitting activation products. However, drill-shavings or pieces cut by means of a plasma arc torch may be collected for further analysis in a laboratory where they can be analyzed in a low-background environment. In general, these materials require no preservation but, based on activity/dose rate levels and sample size and weight, may require proper shielding, engineered packaging, and shipping by a licensed carrier.

10.4.3.2 Biota: Samples of Plant and Animal Products

The release of radionuclides to the environment from normal facility operations or as the result of an accident requires the sampling of a wide variety of terrestrial and aquatic biota. Guidance provided below is directed principally to those responsible for designing a sampling plan, who must make decisions pertaining to the type of samples that should be collected, where and how to collect the samples, and the preferred methods for sample preparation. For most biota, sample preservation usually is achieved by icing samples in the field and refrigeration until receipt by the analytical laboratory.

The specific media that fall under this general category include food, domestic animals (meat and poultry), animal products, game animals, game birds, etc. The field sampling plan should describe the type of processing and preservation required.

Samples of food and certain terrestrial animals are of greatest importance in environmental surveillance because they provide the most direct basis for assessing the radiation dose to man. The principal pathways for radionuclide contamination of food and plants are atmospheric deposition from airborne releases and crop irrigation from rivers, ponds or lakes receiving liquid effluents. Care should also be taken not to select a sampling site that has been fertilized or has been contaminated by runoffs from fertilized soil due to enhanced natural radioactivity content of many fertilizers (ASTM C998).

To determine the dose to a population, pathway analysis may require sampling of food and biota. One example is the analysis of meat from domestic or game animals. Samples from food and biota also may be used to determine radionuclide accumulation in the environment. For example, the analysis of growth rings from trees may indicate when a radionuclide was released into the environment.

Animal feeds also provide important data for determining radionuclide concentrations in the food chain. Foods may be categorized according to the U.S. Department of Agriculture scheme as leafy vegetables, grains, tree-grown fruits, etc., and representative samples from each group may

be selected for analysis. Guidance for procuring or preparing terrestrial samples is provided below.

MEAT, PRODUCE, AND DAIRY PRODUCTS

Meat, poultry, eggs, fresh produce, and other food should be procured from local farmers most likely to have been affected by a singular event. The choice of sample is dependent on the pathway. Meat samples also may be collected at a slaughter house if the origin of the animals can be documented. Local health departments may be able to assist in getting samples. Samples should be placed in sealed plastic bags and appropriately labeled and preserved by means of ice in the field and refrigeration during interim storage prior to delivery to the analytical laboratory. All food samples may be reduced to edible portions (depending on study objective) for analysis in a manner similar to that for human consumption (i.e., remove cores, bones, seeds, other nonedible parts) and weighed as received from the field (i.e., wet weight) within 24 hours. Wet weights are desired, since consumption data are generally on this basis.

For sampling fresh produce, fruits, meats, and other domestic animal products, a local land-use study may be necessary to determine what crops and animals are important in the local diet and where they are produced with respect to the site. Fruit and vegetable samples should be collected near the point of maximum predicted annual ground concentration from airborne releases and from areas that may be contaminated by water into which liquid plant wastes have been discharged (e.g., irrigated crops). Local land usage should be reviewed periodically, as well as current farming and stock-feeding practices at sampling locations.

ANIMAL FEED AND VEGETATION

Crops raised for animal feed and vegetation consumed by grazing farm animals may be sampled. Depending upon radionuclides under investigation and their analytical sensitivities, kilogram quantities of vegetative matter may be needed. The choice of species and sample type must be guided by factors such as exposure pathways, species availability, seasonal growth patterns, soil types, and farming practices.

As in all terrestrial samples, naturally occurring ^{40}K and the uranium and thorium series contribute to the radiation observed. Deposition of such cosmic-ray-produced nuclides as ^{7}Be and fallout from nuclear tests also may be present. Properly selected processed items from commercial sources may be helpful in providing natural and anthropogenic background data.

WILDLIFE

Wild animals that are hunted and eaten may be of interest for potential dose estimates and therefore may require sampling. However, the data from small numbers of samples of wild animals or game birds should be viewed with caution because of their great variation in mobility,

age, and diet. Examples of wildlife that have been used are rabbits and rodents that may feed on and live in a contaminated site.

Wildlife samples can be trapped, acquired from hunters, collected after accidental road kills, or obtained by request to the appropriate state game agency. Wildlife that is relatively rare locally should not be taken as environmental samples. Since the choice of species samples may be crucial to the usefulness of the results, local ecologists and biologists should be consulted to ensure consideration of factors that affect animal radionuclide uptake and retention, such as size, age, sex, feeding locus, and food consumption. An estimate of the radionuclide intake of the animal just before its death may be provided by analyzing the stomach content, especially the rumen in deer. However, the sample must be collected within a brief period (two to four hours) after death.

AQUATIC ENVIRONMENTAL SAMPLES

In addition to natural radionuclides and natural radionuclides enhanced by human activity, there are numerous man-made radionuclides that have the potential for contaminating surface and ground water. The most common of these are fission and activation products associated with reactor operation and fuel cycle facilities. Radioanalysis of aquatic samples may therefore include ^{54}Mn, ^{58}Co, ^{60}Co, ^{65}Zn, ^{95}Zr, ^{90}Sr, ^{134}Cs, ^{137}Cs, and transuranics, such as ^{239}Pu.

When surface and ground waters are contaminated, radionuclides may be transferred through a complex food web consisting of aquatic plants and animals. Aquatic plants and animals, as discussed here, are any species which derive all or substantial portions of their nourishment from the aquatic ecosystem, are part of the human food chain, and show significant accumulation of a radionuclide relative to its concentration in water. Although fish, aquatic mammals, and waterfowl provide a direct link to human exposure, lower members of the food chain also may be sampled.

FLORA

Aquatic biota such as algae, seaweed, and benthic organisms are indicators and concentrators of radionuclides—especially ^{59}Fe, ^{60}Co, ^{65}Zn, ^{90}Sr, and ^{137}Cs—and can be vectors in the water-fish-human food chain. As such, they may be sampled upstream and downstream at locations similar to those described for sediment. Because of their high water content, several kilograms (wet weight) should be collected per sample. The wet weight of the sample should be recorded. Enough of the wet sample should be processed so that sufficient sample remains following the drying process. Both algae (obtained by filtering water or by scraping submerged substrates) and rooted aquatic plants should be sampled.

FISH AND SHELLFISH

For practical reasons, fish and shellfish may be purchased from local sources if the origin can be determined. Samples also can be obtained by pole fishing, netting, or electric shock devices. The sampling plan will describe the processing needed. Samples should include each of the principal edible types in local catches. Several kilograms of each fish sample are usually required; this may be one large fish, but preferably a composite of a number of small ones. Analysis of the edible portions of food fish as prepared for human consumption is of major interest. Fish may be de-boned, if specified in the sampling plan. The whole fish is analyzed if it is used for the preparation of a fish meal for consumption or if only trend indication is required. In a program where fish are the critical pathway, fish are analyzed by species; if less detail is required, several species with similar feeding habits (such as bottom feeders, insectivores, or predators) may be collected and the data grouped.

In large bodies of water, samples from several locations are desirable because of the difficulty in knowing whether a fish caught at a given location had lived there for an extended period. Thus, the presence or absence of a radionuclide in a specific fish does not permit any definite conclusion concerning the presence of the radionuclide in water at that location. For some fish, more specific information concerning their usual location may be available; for example, dams, salinity gradients, and temperature gradients can be effective barriers to their movement. Information on fish age, feeding habits, and the quality of the aquatic environment are desirable to evaluate the significance of any findings.

Shellfish, such as clams, oysters, and crabs, are collected for the same reasons as fish, but have the advantage as indicators of being relatively stationary. Their restricted mobility contributes substantially to the interpretation and application of analytical results to environmental surveillance. Edible and inedible portions of these organisms can be prepared separately.

WATERFOWL

Waterfowl, such as ducks and geese, may also concentrate radionuclides from their food sources in the aquatic environment and serve as important food sources to humans. The migratory patterns and feeding habits of waterfowl vary widely. Some species are bottom feeders and, as such, tend to concentrate those radionuclides associated with sediments such as ^{60}Co, ^{65}Zn, and ^{137}Cs. Others feed predominantly on surface plants, insects, or fish.

Whenever practical, and if time permits, waterfowl should be obtained by hunting, but a trapping procedure may also be used. An important consideration in obtaining a sample from waterfowl is that their exterior surfaces, especially feathers, may be contaminated. It is important to avoid contaminating the "flesh" sample during handling. As with other biota samples, analyses may be limited to the edible portions and should be reported on a wet weight basis. Local game officials or aquatic ecologists may provide valuable information for choosing the proper species.

Caution is advised in the selection of background or control locations for all biota (terrestrial and aquatic) sampled, at least for those species whose mobility and feeding habits may significantly affect the results obtained. Since this mobility makes it difficult to establish upstream/ downstream sampling locations for biota in a manner analogous to those for air, water, or plants, a sound sampling strategy may require the expert advice and direction of local ecologists, and fish and game personnel. Samples from the background locations should be from an ecosystem identical to that of those collected near the site, but unaffected by site effluents.

10.5 Air Sampling

The measurement of airborne radionuclides as gases or particulates provides a means of evaluating internal exposure through the inhalation pathways. The types of airborne radioactivity that may require air sampling are normally categorized as: (1) airborne particulates; (2) noble gases; (3) volatilized halogens (principally radioiodines); and (4) tritiated water. Depending upon the source term and the objectives of the investigation, air sampling may be conducted outdoors as well as indoors on behalf of a variety of human receptors. For example, routine outdoor air samples may be taken for large population groups living within a specified radius of a nuclear facility. On the other end of the spectrum, air samples may be taken for a single person or small group of persons exposed occupationally to a highly localized source of airborne radioactivity.

The purpose of the samples being collected must, therefore, be well defined in terms of sampling location, field sampling equipment, and required sample volumes. Due to the wide range of conditions that may mandate air sampling, and the limited scope of this section, only generic topics of air sampling will be discussed.

10.5.1 Sampler Components

Common components of air sampling equipment include a sample collector (i.e., filter), a sample collector holder, an air mover, and a flow-rate measuring device.

The sample holder should provide adequate structural support while not damaging the filter, should prevent sampled air from bypassing the filter, should facilitate changing the filter, and should facilitate decontamination. A backup support that produces negligible pressure drop should be used behind the filter to prevent filter distortion or deterioration.

If rubber gaskets are used to seal the filter to the backing plate, the gasket should be in contact with the filter along the entire circumference to ensure a good fit.

Air movers or vacuum systems should provide the required flow through the filter and to minimize air flow reduction due to filter loading. Consideration should be given to the use of air movers that compensate for pressure drop. Other factors to consider should include size, power consumption, noise, durability, and maintenance requirements.

Each air sampler should be equipped with a reliable calibrated air flow measuring device with specified accuracy. To calculate the concentrations of any radionuclide in air collected, it is necessary to accurately determine the total volume of air sampled. The planning documents should state who is responsible for making volume corrections. Also, the information needed for half-life corrections for short-lived radionuclides needs to be recorded.

Generally, a parameter of the air mover can be related to flow. If the mean flow during a collection period can be determined, the total volume of air sampled can be readily calculated. Accurate flow measurements and the total integrated sample volume of air can be obtained using a mass flow meter and a totalizer. This direct technique of air flow measurement becomes impractical at remote field locations, due to cost and exposure of the flow meter to harsh environments. Other procedures for the measurement of air flow in sampling systems are reviewed by Lippmann (1989a). The equipment readings (flow rate, volume, etc.) should be recorded by the sample collector.

The collection medium or filter used depends on the physical and chemical properties of the materials to be collected and counted. A variety of particulate filters (cellulose, cellulose-asbestos, glass fiber, membrane, polypropylene, etc.) is available. The type of filter is selected according to needs, such as high collection efficiency, particle-size selectivity, retention of alpha emitters on the filter surface, and the compatibility with radiochemical analysis. The criteria for filter selection are good collection efficiency for submicron particles at the range of face velocities used, high particle and mass loading capacity, low-flow resistance, low cost, high mechanical strength, low-background activity, compressibility, low-ash content, solubility in organic solvents, non-hygroscopicity, temperature stability, and availability in a variety of sizes and in large quantities. The manufacturer's specifications and literature should provide a source for filter collection efficiency. In the selection of a filter material, a compromise must be made among the above-cited criteria that best satisfies the sampling requirements. An excellent review of air filter material used to monitor radioactivity was published by Lockhart and Anderson (1964). Lippmann (1989b) also provides information on the selection of filter materials for sampling aerosols by filtration. See ANSI (1999), Annex D and Table D.1, for criteria for the selection of filters for sampling airborne radioactive particles.

In order to select a filter medium with adequate collection efficiency, it may be necessary to first determine the distribution of size of airborne particulates. Several methods, including impactors (e.g., multistage cascade impactor) and electrostatic precipitators, can be used to classify particle size. Waite and Nees (1973) and Kotrappa et al. (1974) discuss techniques for particle sizing based on the flow discharge perturbation method and the HASL cyclone, respectively. These techniques are not recommended for routine environmental surveillance of airborne particulates, although their use for special studies or for the evaluation of effluent releases should not be overlooked. Specific data on various filter materials, especially retention efficiencies, have been reported by several authors (Lockhart and Anderson, 1964; Denham, 1972; Stafford, 1973; ASTM STP555) and additional information is available from manufacturers.

10.5.2 Filter Selection Based on Destructive Versus Non-destructive Analysis

Pure cellulose papers are useful for samples to be dissolved and analyzed radiochemically, but the analytical filter papers used to filter solutions are inefficient collectors for aerosols and clog easily. Cellulose-asbestos filter papers combine fairly high efficiency, high flow rates, high mechanical strength, and low pressure drops when loaded. They are very useful for collecting large samples but present difficulties in dissolution, and their manufacture is diminishing because of the asbestos. Fiberglass filters can function efficiently at high flow rates, but require fluoride treatment for dissolution and generally contain sufficient radioactive nuclides to complicate low-activity analysis. Polystyrene filters are efficient and capable of sustaining high air flow rates without clogging. They are readily destroyed for analysis by ignition (300° C) or by wet washing with oxidizing agents, and also are soluble in many organic liquids. They have the disadvantage of low mechanical and tensile strength, and they must be handled carefully. Membrane filters are excellent for surface collection efficiency and can be used for direct alpha spectrometry on the filter. However, they are fragile and suffer from environmental dust loading. An alternative choice for radionuclides in the environment is the polypropylene fiber filter, Dynaweb Grade DW7301L. Filters come in two sizes: a 20.32 cm circle and a 20.32 cm x 25.40 cm rectangle. The filter is composed of a 100 percent polypropylene web that is 100 percent binderless. Three layers of this web are collated and sandwiched between two sheets of a protective DuPont Reeme (100 percent polyester) scrim.

10.5.3 Sample Preservation and Storage

Since particulate air samples are generally dry samples that are chemically and physically stable, they require no preservation. However, care must be exercised to avoid loss of sample from the filter medium and the cross contamination among individual samples. A common method is to fold filters symmetrically so that the two halves of the collection surface are in contact. Filters should be stored in individual envelopes that have been properly labeled. Filters may also be stored in special holders that attach on the filter's edge outside of the collection surface. When background levels of ^{222}Ra and ^{220}Ra progeny interfere with evaluation of alpha air samples, a holdup time of several hours may be required before samples are counted. Corrections or determinations can also be made for the contribution of radon or thoron progeny present on a filter (Setter and Coats, 1961).

10.5.4 Special Cases: Collection of Gaseous and Volatile Air Contaminants

Prominent radionuclides that may exist in gaseous states include noble gases, ^{14}C as carbon dioxide or methane, ^{3}H as water vapor, and volatilized radioiodines. (Radon is discussed in Section 10.5.5.)

10.5.4.1 Radioiodines

The monitoring of airborne iodine, such as ^{129}I and ^{131}I, may be complicated by the probable existence of several species, including particulate iodine or iodine bound to foreign particles, gaseous elemental iodine, and gaseous non-elemental compounds of iodine. A well-designed sampling program should be capable of distinguishing all possible iodine forms. While it may not always be necessary to differentiate between the various species, care should be taken so that no bias can result by missing one or more of the possible species. See ANSI (1999) Annex C.3, for information on collection media for radioiodine.

In addition to the problems noted above, charcoal cartridges (canisters) for the collection of radioiodine in air are subject to channeling. Hence, they should be carefully checked before operation in the field (analogous to DOP testing of high efficiency particulate air (HEPA) filters *in situ*) or several should be mounted in series to prevent loss of iodine. Too high a sampling rate reduces both the collection efficiency and retention time of charcoal filters, especially for the non-elemental forms of iodine (Keller et al., 1973; Bellamy, 1974). The retention of iodine in charcoal is dependent not only on charcoal volume, but also the length of the charcoal bed. Typical air flow rates for particulate sampling of 30 to 90 L/min (1 to 3 ft^3/min) are normally acceptable for environmental concentrations of radioiodine. The method proposed by the Intersociety Committee (APHA, 1972) for ^{131}I concentrations in the atmosphere involves collecting iodine in its solid and gaseous states with an "absolute" particulate filter in series with an activated charcoal cartridge followed by gamma spectrometric analysis of the filter and cartridge. The Intersociety-recommended charcoal cartridges are 5/8 in. diameter by 1.5 in. deep containing 3 g of 12 to 30 mesh KI-activated charcoal. The minimum detectable level using the Intersociety method is 3.7×10^{-3} Bq/m^3 (0.1 pCi/m^3). Larger cartridges will improve retention, permitting longer sampling periods. A more sensitive system has been described by Baratta et al. (1968), in which concentrations as low as 0.037 Bq/m^3 (0.01 pCi/mL) of air are attainable.

For the short-lived radioiodines (mass numbers 132, 133, 135), environmental sampling is complicated by the need to obtain a sufficient volume for analysis, while at the same time, retrieving the sample soon enough to minimize decay (with half-lives ranging from two hours to 31 hours). Short period (grab) sampling with charcoal cartridges is possible, with direct counting of the charcoal as soon as possible for gamma emissions, but radon and thoron will affect detection levels.

Because of the extremely long half-life and normally low environmental concentrations, ^{129}I determinations must usually be performed by neutron activation or mass spectrometry analysis after chemical isolation of the iodine. For concentrations about 3×10^{-10} μCi/mL, liquid scintillation counting can be used after solvent extraction (Gabay et al., 1974).

10.5.4.2 Gases

Sampling for radioactive gases is either done by grab sample that employs an evacuated chamber or by airflow through a medium such as charcoal, water, or a variety of chemical absorbers. For example, radioactive CO_2 is most commonly extracted by passing a known volume of air through columns filled with 3 M NaOH solution. After the NaOH is neutralized with sulfuric acid, the CO_2 is precipitated in the form of $BaCO_3$, which then can be analyzed in a liquid scintillation counter (NCRP,1985).

Because noble gases have no metabolic significance, and concern is principally limited to external exposure, surveillance for noble gases is commonly performed by ambient dose rate measurements. However, the noble gases xenon and krypton may be extracted from air by adsorption on activated charcoal (Scarpitta and Harley, 1990). However, depending upon the analytical method and instrumentation employed, significant interference may result from the presence of naturally occurring radioactive gases of ^{222}Rn and ^{220}Rn.

10.5.4.3 Tritium Air Sampling

In air, tritium occurs primarily in two forms: as water vapor (HTO) and as hydrogen gas (HT). Tritiated organic compounds in the vapor phase or attached to particulate matter occur only occasionally. To measure tritium as HT or in tritiated organic, the gas phase can be oxidized, converting the tritium to HTO before desiccation and counting. For dosimetric purposes, the fraction present as HT can usually be neglected, since the relative dose for a given activity concentration of HTO is 400 times that for HT (NCRP, 1978). However, if HT analysis is required, it can be removed from the atmosphere by oxidation to water (HTO) using CuO/MnO_2 at 600° C (Pelto et al., 1975), or with air passed over platinum alumina catalyst (Bixel and Kershner 1974). These methods also oxidize volatile tritiated organic compounds to yield tritiated water (ANSI, 1999, Annex H).

A basic system for sampling HTO consists of a pump, a sample collector, and a flow-measuring or flow-recording device. Air is drawn through the collector for a measured time period at a monitored flow rate to determine the total volume of air sampled. The total amount of HTO recovered from the collector is divided by the total volume of air sampled to determine the average HTO-in-air concentration of the air sampled. In some sampler types, the specific activity of the water collected is measured and the air concentration is determined from the known or measured humidity. Some common collectors are cold traps, tritium-free water, and solid desiccants, such as silica gel, DRIERITE™, or molecular sieve.

Cold traps are usually made of glass and consist of cooled collection traps through which sample air flows. The trap is cooled well below the freezing point of water, usually with liquid nitrogen. The water vapor collected is then prepared for analysis, usually by liquid scintillation counting. Phillips and Easterly (1982) have shown that more than 95 percent HTO collection efficiency can

be obtained using a single cold trap. Often a pair of cold traps is used in series, resulting in a collection efficiency in excess of 99 percent.

Gas-washing bottles (i.e., "bubblers") filled with an appropriate collecting liquid (usually tritium-free water) are used quite extensively for collecting HTO from air. HTO in the sample gas stream "dissolves" in the collecting liquid. For the effective collection rate to remain the same as the sample flow rate, the specific activity of the bubbler water must be negligible with respect to the specific activity of the water vapor. Thus, the volume of air that can be sampled is ultimately limited by the volume of water in the bubbler. However, except when sampling under conditions of very high humidity, sample loss (dryout) from the bubbler usually limits collection time rather than the attainment of specific activity equilibrium. Osborne (1973) carried out a thorough theoretical and experimental evaluation of the HTO collection efficiency of water bubblers over a wide range of conditions.

The use of silica gel as a desiccant to remove moisture from air is a common technique for extracting HTO. The advantage of using silica gel is that lower HTO-in-air concentrations can be measured, since the sample to be analyzed is not significantly diluted by an initial water volume, which occurs when a liquid-sampling sink is used. Correcting for dilution is discussed in Rosson et al. (2000).

10.5.5 Radon

There are three isotopes of radon in nature: ^{222}Rn is a member of the ^{238}U decay chain; ^{220}Rn is a member of the ^{232}Th decay chain; and ^{219}Rn is a member of the ^{235}U decay chain. Because of the small relative abundance of the parent nuclides and the short half-lives of ^{220}Rn (55 seconds) and ^{219}Rn (4 seconds), the term "radon" generally refers to the isotope ^{222}Rn. Owing to its ubiquitous presence in soils, uranium mill tailings, underground mines, etc., and the health risks to large populations and occupational groups, radon is perhaps the most studied radionuclide.

Consequently, many reports and articles have been published in the scientific literature dealing with the detection methods and health risks from radon exposures. Many of them appear in publications issued by the EPA, DOE, NCRP, NAS, and in radiation-related journals, such as the journals *Health Physics* and *Radiation Research*. Given the voluminous amount of existing information, only a brief overview of the sampling method can be presented here.

10.5.5.1 Radon Sampling Methods

Quantitative measurements of radon gas and its short-lived decay products can be obtained by several techniques that are broadly categorized as grab sampling, continuous radon monitoring, and integrative sampling. Each method imposes unique requirements that should be followed carefully. The U.S. EPA Radon Measurement Proficiency (RMP) Program should be consulted for current guidance for sample collection (EPA, 1992; EPA,1993). Information is available on

the RMP home page at www.epa.gov/radonpro/index.htm. Working with the Radon Proficiency Program (RPP) is described in a separate handbook (EPA, 1996). A description of additional sampling methods and materials is also presented in EPA (1994) and Cohen (1989).

In general, EPA's protocols specify that radon sampling and measurements be made under standardized conditions when radon and its progeny are likely to be at their highest concentrations and maximum equilibrium. For indoor radon measurement, this implies minimum building ventilation through restrictions on doors, windows, HVAC systems, etc. Also sampling should not take place during radical changes in weather conditions. Both high winds and rapid changes in barometric pressure can dramatically alter a building's natural ventilation rate. Although recommended measurements are likely to generate higher than actual average concentrations, the benefit of a standardized sampling condition is that it is reproducible, least variable, and moderately conservative. Brief descriptions of the basic techniques used to sample air for radon and its progeny are provided below.

GRAB SAMPLING

The term "grab sampling" refers to very short-term sampling. This method consists of evaluating a small volume of indoor air for either radon or radon decay product concentration. In the radon grab sampling method, a sample of air is drawn into and subsequently sealed in a flask or cell that has a zinc sulfide phosphor coating on its interior surfaces. One surface of the cell is fitted with a clear window that is put in contact with a photomultiplier tube to count light pulses (scintillations) caused by alpha disintegrations from the sample interacting with the zinc sulfide coating. The number of pulses is proportional to the radon concentration in the cell. The cell is counted about four hours after filling to allow the short-lived radon decay products to reach equilibrium with the radon. The results are corrected to compensate for decay during the time between collection and counting, and for decay during counting.

Several methods for performing such measurements have been developed. However, two procedures that have been most widely used with good results are the Kusnetz procedure and the modified Tsivogiou procedure. In brief, the Kusnetz procedure (Kusnetz, 1956; ANSI, 1973) may be used to obtain results in working levels (WL) when the concentration of individual decay products is not important. Decay products in up to 100 liters of air are collected on a filter in a five-minute sampling period. The total alpha activity on the filter is counted any time between 40 and 90 minutes after sampling is completed. Counting can be done using a scintillation-type counter to obtain gross alpha counts for a selected counting time. Counts from the filter are converted to disintegrations using the appropriate counter efficiency. The disintegrations from the decay products may be converted into working levels using the appropriate "Kusnetz factor" for the counting time used.

The Tsivogiou procedure may be used to determine both WL and the concentration of the individual radon decay products. Sampling is the same as in the Kusnetz procedure. However,

the filter is counted three separate times following collection. The filter is counted between 2 and 5 minutes, 6 and 20 minutes, and 21 and 30 minutes after sampling is complete. Count results are interpreted by a series of equations that calculate concentrations of the three radon decay products and WL.

The advantages of grab sampling are that the analysis time is relatively short, results are available within a short time, and conditions during the measurement are known to the sampler. In addition, grab sampling does not provide a long-term average and house conditions must be controlled for 12 hours prior to measurement.

CONTINUOUS RADON MONITOR

A continuous radon monitor (CRM) samples the ambient air by pumping air into a scintillation cell after passing it through a particulate filter that removes dust and radon decay products. As the radon in the air decays, the ionized radon decay products plate out on the interior surface of the scintillation cell. As the radon decays, the alpha particles strike the coating on the inside of the cell, causing scintillations. The scintillations are detected by the photomultiplier tube in the detector, which generates electrical signals. The signals are processed and the results are either stored in the memory of the CRM or printed on paper tape by the printer. The CRM must be calibrated in a known environment to obtain the conversion factor used to convert count to radon concentration.

The CRM may be a flowthrough-cell type or a periodic-fill type. In the flowthrough-cell type, air flows continuously into and through the scintillation cell. The periodic-fill type fills the cell once during each preselected time interval, counts the scintillations, then begins the cycle again.

An analogous device to the continuous radon monitor is the Continuous Working Level Monitor (CWLM). This device filters air at a low flow rate of about 0.2 to one liter per minute and measures the amount of radon decay products on the filter medium. An alpha detector, such as a diffused-junction or surface-barrier detector, counts the alpha particles produced by the radon decay products as they decay on the filter. The detector is normally set to detect alpha particles with energies between 2 and 8 meV. The alpha particles emitted from the radon decay products ^{218}Po and ^{214}Po are the significant contributors to the events that are measured by the detector. The event count is directly proportional to the number of alpha particles emitted by the radon decay products on the filter. The unit typically contains a microprocessor that stores the number of counts and elapsed time. The unit can be set to record the total counts registered over specified time periods. The unit must be calibrated in a calibration facility to convert count rate to working level (WL) values. This may be done initially by the manufacturer and should be done periodically thereafter by the operator.

INTEGRATING SAMPLING DEVICES

By far, the most common technique for measuring radon is by means of integrating devices. Integrating devices, like the charcoal canister and the Electret-Passive Environmental Radon Monitor, are commonly employed as short-term integrating devices (two to seven days), while alpha track detectors are commonly used to provide measurements of average radon levels over periods of weeks to months.

CHARCOAL CANISTERS

Charcoal canisters (CC) are passive devices requiring no power to function. The passive nature of the activated charcoal allows continual adsorption and desorption of radon. During the measurement period, the adsorbed radon undergoes radioactive decay. Therefore, the technique does not uniformly integrate radon concentrations during the exposure period. As with all devices that store radon, the average concentration calculated using the mid-exposure time is subject to error if the ambient radon concentration adsorbed during the first half of the sampling period is substantially higher or lower than the average over the period. For a 2 to 7 day exposure period, the minimum detectable concentration (MDC) should be 18.5 Bq/m^3 (0.5 pCi/L) or less (EPA, 1989). This detection level can normally be achieved with a counting time of up to 30 minutes. This MDC should be calculated using the results of charcoal background determinations. The coefficient of variation should not exceed 10 percent (1 sigma) at radon concentrations of 148 Bq/m^3 (4 pCi/L) or greater (EPA, 1989). This precision should be monitored using the results of duplicate canister analyses. CCs can achieve an average coefficient of variation of less than five percent at concentrations of 148 Bq/m^3 (4 pCi/L) or greater.

ELECTRET-PASSIVE ENVIRONMENTAL RADON MONITORS

Electret-passive environmental radon monitors (E-perms) require no power and function as true integrating detectors that measure the average concentration during the exposure period. E-PERMS contain a permanently charged Electret (an electrostatically charged disk of Teflon) that collects ions formed in the chamber by radiation emitted from radon decay products. When the device is exposed, radon diffuses into the chamber through filtered openings. Ions that are generated continuously by the decay of radon and radon decay products are drawn to the surface of the electret and reduce its surface voltage. The amount of voltage reduction is related directly to the average radon concentration present during the exposure period. There are both short-term (2 to 7 days) and long-term (1 to 12 months) E-PERMS that are marketed currently. The thickness of the electret affects the usable measurement period. For a 7-day exposure period using a short-term E-PERM, as well as for a long-term E-PERM, the MDC is about 11.1 Bq/m^3 (0.3 pCi/L) (EPA, 1989). The coefficient of variation should not exceed 10 percent (1 sigma) at radon concentrations of 148 Bq/m^3 (4 pCi/L) or greater. This precision should be verified by using results of duplicate detector analysis.

ALPHA TRACK DETECTORS

An alpha track detector (ATD) consists of a small piece of plastic or film enclosed in a container with a filter-covered opening. Radon diffuses through the filter into the container and alpha particles emitted by radon and its decay products strike the detector and produce submicroscopic damage tracks. At the end of the measurement period, the detectors are returned to a laboratory. Plastic detectors are placed in a caustic solution that accentuates the damage tracks so they can be counted using a microscope or an automated counting system. The number of tracks per unit area is correlated to the radon concentration in air, using a conversion factor derived from data generated at a calibration facility. The number of tracks produced per unit time is proportional to the radon concentration, so an ATD functions as a true integrating detector and measures the average concentration over the measurement period. The MDC and precision of an ATD system is dependent upon the tracks counted and, therefore, the area of the detector that is analyzed. With present ATDs, routine counting achieves a MDC of 6,660 Bq/m^3-days (180 pCi/L-days). The coefficient of variation (precision) should be monitored using the results of duplicate detectors. The coefficient of variation should not exceed 20 percent (1 sigma) at radon concentrations of 148 Bq/m^3 (4 pCi/L) or greater (EPA, 1989).

10.5.5.2 Selecting a Radon Sampling Method Based on Data Quality Objectives

The choice from among the sampling methods described above depends on whether the measurement is intended as a quick screening measurement or as a measurement that determines average exposure. In practice, the choice of a measurement system often is dictated by availability. If alternative systems are available, the cost or duration of the measurement may become the deciding factor. Each system has its own advantages and disadvantages, and the investigator must exercise some judgment in selecting the system best suited to the DQOs of the investigation.

There are, however, some general guidelines concerning standardized measurement conditions and quality assurance objectives which apply to all measurement techniques. The following elements of quality assurance should be included in any measurement program: detector calibrations, replicate measurements, background measurements, and routine sensitivity checks.

Detector calibrations are measurements made in a known radon environment, such as a calibration chamber. Detectors requiring laboratory readout, such as charcoal canisters and alpha-track detectors, should be exposed in the calibration chamber and then analyzed. Instruments providing immediate results, such as continuous working-level monitors and continuous radon monitors, should be operated in a chamber to establish calibration.

There are two types of calibration measurements that should be made for alpha-track detectors and charcoal canisters. The first measurements determine and verify the conversion factors used to derive the concentration results. These measurements, commonly called spiked samples, are

done at the beginning of the measurement program and periodically thereafter. The second calibration measurements monitor the accuracy of the system. These are called blind calibration measurements and consist of detectors that have been exposed in a radon calibration chamber. The detectors are not labeled as such when sent to a processing laboratory.

Background measurements, or blanks, should also be conducted. Such measurements should be made using unexposed passive detectors, or should be instrument measurements conducted in very low (outdoor) radon concentration environments and separated from the operating program. Generally, these should be equivalent in frequency to the spiked samples and should also not be identified as blanks when submitted for analysis to external laboratories. In addition to these background measurements, the organization performing the measurements should calculate the minimum detectable concentration MDC for the measurement system. This MDC is based on the system's background and can restrict the ability of some measurement systems to measure low concentrations.

Duplicate measurements provide an estimate of the precision of the measurement results. Duplicate measurements should be included in at least 10 percent of the samples. If enough measurements are made, the number of duplicates may be reduced, as long as enough are used to analyze the precision of the method.

A quality assurance program should include a written plan for satisfying the preceding objectives. A system for monitoring the results of the four types of quality assurance measurements should also be maintained.

Calibrated radon detection devices and on-site measurements can also be obtained under contract from commercial vendors who have demonstrated their proficiency in measuring radon and radon decay products, and who have had their quality assurance programs assessed by the EPA or state agencies.

10.6 Wipe Sampling for Assessing Surface Contamination

Surface contamination falls into two categories: fixed and loose. The wipe test (also referred to as "swipes" or "smears") is the universally accepted technique for detecting removable radioactive contamination on surfaces (Section 12.5). It is often a stipulation of radioactive materials licenses and is widely used by laboratory personnel to monitor their work areas, especially for low-energy radionuclides that are otherwise difficult to detect with hand-held survey instruments. A comprehensive history of "Use of Smears for Assessing Removable Contamination" is presented by Frame and Abelquist (1999).

The U.S. Nuclear Regulatory Commission (NRC, 1981) suggests that 100 cm^2 areas be wiped and lists acceptable levels for surface contamination. However, NRC neither recommends the collection device nor the manner in which to conduct such surveys, relying instead on

suggestions by the National Committee on Radiation Protection (1964) and the National Council on Radiation Protection and Measurements (1978).

10.6.1 Sample Collection Methods

10.6.1.1 Dry Wipes

Smears for removable surface activity are obtained by wiping an area of approximately 100 cm^2 using a dry filter paper, such as Whatman 50 or equivalent, while applying moderate pressure. A 47 mm diameter filter is typically used, although for surveys for low-energy beta emitters, smaller sizes may be more appropriate because they can be placed directly into a liquid scintillation vial for counting. Small pieces of wipes occasionally are used for smears for tritium (Slobodine and Grandlund, 1974). A smear for removable contamination is obtained at each location of direct surface activity measurement.

For surveys of small penetrations, such as cracks or anchor-bolt holes, cotton swabs are used to wipe the area of concern. Samples (smears or swabs) are placed into envelopes or other individual containers to prevent cross-contamination while awaiting analysis. Smears for alpha and medium- or high-energy beta activity can be evaluated in the field by counting them on an integrating scaler unit with appropriate detectors; the same detectors utilized for direct measurements may be used for this purpose. However, the more common practice is to return the smears to the laboratory, where analysis can be conducted using more sensitive techniques. The most common method for analyzing wipe samples is to use a proportional counter. For very low-energy beta emissions, wipe samples are commonly analyzed by liquid scintillation counting.

10.6.1.2 Wet Wipes

Although dry wipes are more convenient to handle, and there are fewer chances of cross contamination, a general limitation of dry wipes is their low recovery of surface contamination. The low recovery using dry wipes is due to the higher affinity for the surface by the contaminant than for the filter paper. Several studies have shown that for maximum sensitivity, a wipe material moistened with a suitable solvent may be indicated. For example, Ho and Shearer (1992) found that alcohol-saturated swabs were 100 times more efficient at removing radioactivity than dry swabs.

In another study, Kline et al. (1992) assessed the collection efficiency of wipes from various surfaces that included vinyl floor tile, plate glass, and lead foil. Two different collection devices, cotton swabs and 2.5 cm diameter glass fiber filter disks, were evaluated under various collection conditions. Dry wipes were compared to collections made with the devices dampened with different amounts of either distilled H_2O, 70 percent ethanol, or a working-strength solution of a multipurpose laboratory detergent known to be effective for removing contaminants from laboratory glassware (Manske et al., 1990).

The entire area of each square was manually wiped in a circular, inwardly-moving motion with consistent force. The collection capacity of each device was estimated by wiping progressively larger areas (multiple grids) and comparing the measured amounts of radioactivity with the amounts placed on the grids.

Collection efficiency varied with both the wipe method and the surface wipe. Contamination was removed most readily from unwaxed floor tile and glass; lead foil released only about one-half the radioactivity. Stainless steel, another common laboratory surface, has contamination retention properties similar to those of glass.

In most cases, collection was enhanced by at least a factor of two after dampening either the swabs or filter disks with water. Dampening with ethanol or the detergent produced removals that were statistically indistinguishable from samples dampened with an equal amount of water.

The filter disks had a higher collection capacity for removable contaminants than cotton swabs, nearly doubling the radioactivity removed for each doubling of surface area wiped. Variability within all methods was high, with coefficients of variation ranging from 2 to 30 percent.

For the moistened wipes, wipe efficiency depended on three factors, including the polarity of the solvent, the polarity of the contaminant being measured, and the affinity of the compound for the contaminated surface. For a solvent to readily dissolve a compound (i.e., remove it from the surface), the solvent and the compound must have similar polarities. Nonpolar solvents include ethyl acetate and petroleum ether; for polar solvents, water or methanol may be used (Cambell et al., 1993). There are other factors that influence the affinity of a compound for a surface, including porosity of the surface and available binding sites on the surface. One important factor which influences binding capacity is the type of treatment that a surface has received. When working with a surface treated with a nonpolar wax, such as that used on floor tile, a nonpolar compound will be adsorbed to the surface, which further limits recovery. In contrast, recovery from absorbent surfaces, such as lab bench paper or untreated wood, may give poor recoveries due to the porous nature of the surface.

10.6.2 Sample Handling

Filter paper or other materials used for wipe tests in the field should be placed in separate containers that prevent cross contamination during transport and allow for labeling of each sample. Plastic bags, paper or glassine envelopes, and disposable plastic petri dishes are containers typically used to store and transport wipe samples. Field workers can use plastic or rubber gloves and forceps when applying the wipe material to a surface and during handling as each wipe is placed into a container. Protection of the sample wipe surface is the main concern when a wipe must be placed in a container for transport. If a scintillation vial or planchet will be used in the lab, then a field worker may put wipes directly into them. Planchets containing loose or self-sticking wipes can also be put into self-sealing plastic bags to separate and protect the

integrity of the sample's surface. Excessive dust and dirt can cause self adsorption or quenching, and therefore should be minimized.

To maintain constant geometry in an automatic proportional counter, it is important that the wipe remain flat during counting. Additionally, material that will curl can jam the automatic counter and cause cross contamination or even destroy the instrument window. When it is necessary to do destructive analysis on the wipe, it is critical that the wipe can easily be destroyed during the sample preparation step, and that the residue not cause interference problems.

When wipes are put directly into liquid scintillation cocktail, it is important that the wipe not add color or react with the cocktail. For maximum counting efficiency, as well as reproducibility, the wipe should either dissolve or become translucent in the cocktail.

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11 SAMPLE RECEIPT, INSPECTION, AND TRACKING

11.1 Introduction

This chapter provides guidance on laboratory sample receiving and screening, inspecting, documenting custody, and assigning laboratory tracking numbers. These topics are presented in a sequentially in this chapter, but they may be done in a different order. The chapter is directed primarily at laboratory personnel (as are all of the Part II chapters), although the Project Manager and field personnel need to be aware of the steps involved in sample receipt, inspection, and tracking. For the purposes of MARLAP, the "sample receipt" process includes the screening of the package and sample containers for radiological contamination. "Sample inspection" is used to check the physical integrity of the package and samples, to confirm the identity of the sample, to confirm field preservation (if necessary), and to record and communicate the presence of hazardous materials. "Laboratory sample tracking" is a process starting with sample log-in and assignment of a unique laboratory tracking number to be used to account for the sample through analyses, storage, and shipment. Laboratory tracking continues the tracking that was initiated in the field during sample collection.

Figure 11.1 presents an overview of the topics discussed in this chapter. Note that the flow diagram in the field sample preparation chapter (Chapter 10, *Field and Sampling Issues that Affect Laboratory Measurements*) leads into sample receipt. This chapter focuses on sample receipt, inspection, and tracking of samples in the laboratory because these are the three modes of initial control and accountability. Sample receipt and inspection activities need to be done in a timely manner to allow the laboratory and field personnel to resolve any problems (e.g., insufficient material collected, lack of field preservation, etc.) with the samples received by the laboratory as soon as is practical. An effective interface between field personnel and the laboratory not only facilitates problem resolution but also prevents unnecessary delays in the analytical process.

Other relevant issues, including the laboratory's license conditions and proper operating procedures are also noted because these topics are linked to receipt, inspection, and tracking ities. The end result of the sample receipt and inspection activities is to accept the samples as received or to perform the necessary corrective action (which may include rejecting samples).

Health and safety information is not presented but can be found in NRC (1998a; 1998b).

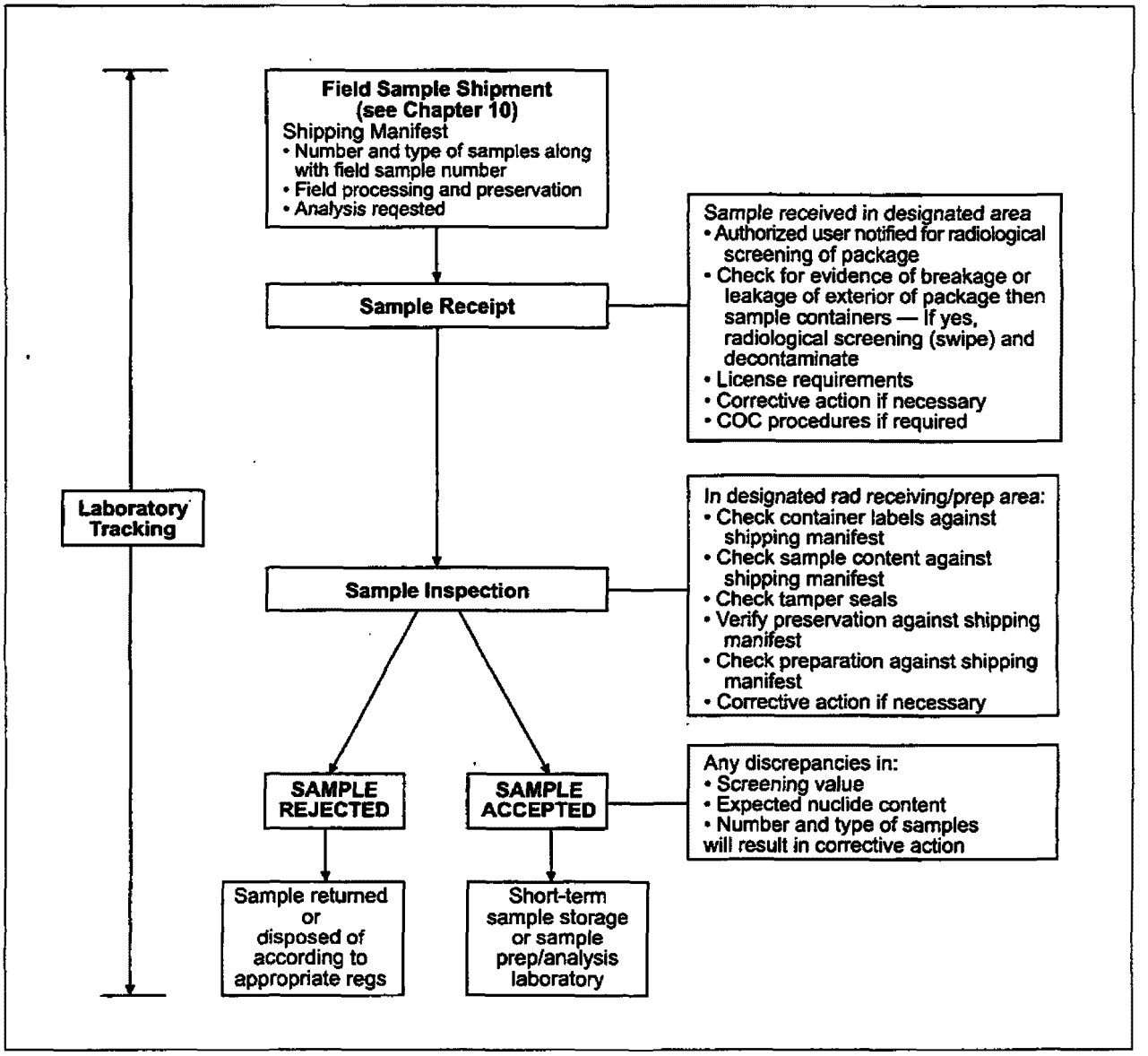

FIGURE 11.1 — Overview of sample receipt, inspection, and tracking

11.2 General Considerations

11.2.1 Communication Before Sample Receipt

Before the samples are received, the laboratory should know the relative numbers of samples that will be received within a specific timeframe and the types of analyses that are expected for the samples. Laboratory personnel should be provided with a contact in the field and with means of contacting the person (telephone, FAX, e-mail). Communication between laboratory personnel and project staff in the field allows the parties to coordinate activities, schedules, and sample receipt. In particular, the Project Manager should provide to the laboratory special instructions regarding the samples before shipment of samples. This information serves to notify the laboratory of health and safety concerns and provides details that will affect analytical procedures, sample disposition, etc. For example, without this communication, a laboratory might receive a partial shipment and not realize that samples are missing. Furthermore, advance communications allow laboratory staff to arrange for special handling or extra space for storage should the need arise.

Planning for the samples to be received at the laboratory starts during the development of the appropriate plan document and the statement of work (SOW) and continues through the communication between the project staff in the field and the laboratory. For example, the laboratory could pre-label and bar-code the appropriate containers to be used in the field. This process would assist in assigning appropriate sample numbers for the laboratory tracking system, which starts with sample receipt. The laboratory should instruct the field staff to place the shipping manifest on the inside of the cooler lid for easy access and to include any other pertinent information (field documentation, field screen information, etc.).

11.2.2 Standard Operating Procedures

A laboratory should have standard operating procedures (SOPs) for laboratory activities related to sample receipt, inspection, and tracking. Some typical topics that might be addressed in laboratory SOPs are presented in Table 11.1. For example, the laboratory should have an SOP that describes what information should be included in the laboratory sample tracking system. Laboratory SOPs should describe chain-of-custody procedures giving a comprehensive list of the elements in the program such as signing the appropriate custody forms, storing samples in a secure area, etc. (ASTM D4840; ASTM D5172; EPA, 1995).

TABLE 11.1 —Typical topics addressed in standard operating procedures related to sample receipt, inspection, and tracking

Sample Receipt:	• Order and details for activities associated with receiving shipments of samples. • Screening methods.
Inspection:	• pH measurement instructions. • Confirm sample identification. • Assign samples to laboratory information management system (LIMS). • Check physical integrity. • Identify/manage hazardous materials.
Tracking:	• Ensure proper identification of samples throughout process. • Procedures to quickly determine location and status of samples within laboratory. • Maintain chain of custody and document sample handling during transfer from the field to the laboratory, then within the laboratory.
Custodian:	• Execution of responsibilities of the sample custodian.
Forms/Labels:	• Examples of forms and labels used to maintain sample custody and document sample handling in the lab.

The laboratory needs to establish corrective action guidelines (Section 11.3.3) as part of every SOP for those instances when a nonconformance is noted. Early recognition of a nonconformance will allow the Project Manager and the laboratory more options for a quick resolution.

11.2.3 Laboratory License

Laboratory facilities with a few exceptions (e.g., certain DOE National Laboratories and DOD laboratories) that handle radioactive materials are required to have a radioactive materials license issued by the NRC or the Agreement State in which the laboratory operates. The radioactive materials license lists the radionuclides that the laboratory can possess, handle, and store. In addition, the license limits the total activity of specific radionuclides that can be in the possession of the laboratory at a given time.

The laboratory needs to have specific information from the field staff to make sure they can receive samples with the particular radionuclides expected to be present in the samples and that the laboratories have the proper radioactive materials license. The information needed includes the results of radiological field screening measurements. Both the laboratory and the Project Manager need to be aware of the type of radionuclide(s) in the samples and the total number of samples to be sent to the laboratory (this should be included in the appropriate plan document and SOW prior to sampling).

The laboratory is required by the license to maintain a current inventory of certain radioactive materials present in the facility. The radioactive materials license also requires the laboratory to develop and maintain a *radiation protection plan* (NRC, 1998b) that states how radioactive samples will be received, stored, and disposed. The laboratory will designate an *authorized user* (NRC, 1998b) to receive the samples. A Radiation Safety Officer (RSO) may be an authorized user but not always. NRC (1998b) gives procedures for the receipt of radioactive samples during working hours and non-working hours; part of these procedures are as follows:

> During normal working hours, immediately upon receipt of any package of licensed material, each package must be visually inspected for any signs of shipping damage such as crushed or punctured containers or signs of dampness. Any obvious damage must be reported to the RSO immediately. Do not touch any package suspected of leaking. Request the person delivering the package to remain until monitored by the RSO.
>
> Any packages containing radioactive material that arrive between (state times, e.g., 4:30 p.m. and 7:00 a.m. or on Saturdays or Sundays) shall be signed for by the security guard (or other designated trained individual) on duty and taken immediately to the designated receiving area. Security personnel (or other designated trained individual) should unlock the door, place the package in the designated secured storage area and re-lock the door.
>
> Since certain packages of licensed material will have detectable external radiation, they should be sent immediately to a designated storage area, where they will be checked for contamination and external radiation level as soon as practical. They should not be allowed to remain in the receiving area any longer than necessary, as they may be a source of exposure for receiving personnel.

11.2.4 Sample Chain-of-Custody

"Sample chain-of-custody" (COC) is defined as a process whereby a sample is maintained under physical possession or control during its entire life cycle, that is, from collection to disposal (ASTM D4840—see Chapter 10). The purpose of COC is to ensure the security of the sample throughout the process. COC procedures dictate the documentation needed to demonstrate that COC is maintained. When a sample is accepted by the laboratory it is said to be in the physical possession or control of the laboratory. ASTM D4840 says that a sample is under "custody" if it is in possession or under control so as to prevent tampering or alteration of its characteristics.

If the samples are transferred under COC the relinquisher and the receiver should sign the appropriate parts of the COC form with the date and time of transfer. After receipt and inspection the samples should be kept in a locked area or in an area with controlled access.

COC is not a requirement for all samples. COC is most often required when the sample data may be used as legal evidence. The project plan should state whether COC will be required. The paperwork received with the samples should also indicate whether COC has been maintained from the time of collection and must be maintained in the laboratory. If the laboratory has been informed that COC procedures should be followed, but it appears that appropriate COC procedures have not been followed (before or after sample receipt at the laboratory) or there are signs of possible sample tampering when the samples arrive, the Project Manager should be contacted. The problem and resolution should be documented. Additional information on COC can be found in EPA (1985).

11.3 Sample Receipt

Laboratory sample receipt occurs when a package containing samples is accepted, the package and sample containers are screened for radiological contamination, and the physical integrity of the package and samples is checked. Packages include the shipping parcel that holds the smaller sample containers with the individual samples (see Section 11.3.2 on radiological screening). Also note that topics and activities covered in Section 11.3 appear in a sequence but, in many cases, these activities are performed simultaneously during initial receiving activities (i.e., package screening and observation of its physical integrity).

11.3.1 Package Receipt

Packages can be accepted only at a designated receiving area. Packages brought to any other location by a carrier should be redirected to the appropriate receiving area. All packages labeled RADIOACTIVE I, II, or III require immediate notification of the appropriate *authorized user* (NRC, 1998b).

A sample packing slip or manifest is required and must be presented at the time of receipt, and the approximate activity of the shipment should be compared to a list of acceptable quantities. If known, the activity of each radionuclide contained in the shipment must be reviewed relative to the total amount of that radionuclide currently on site to ensure that the additional activity will not exceed that authorized by the NRC or Agreement State in the laboratory's license.

Screening measures described in Section 11.3.2 may indicate that the samples are more radioactive than expected and that the radiation license limit may be exceeded. The laboratory should take extra precautions with these samples, but the screening results should be verified. The Federal, State, or local agency should be contacted immediately when verified license limits are exceeded. The laboratory must respond quickly to stay in compliance with their license.

If the package is not accepted by the laboratory, the laboratory should follow corrective-action procedures prescribed in the radiation materials license, the appropriate plan document (if this is a reasonable possibility for the project), and the laboratory's SOPs.

11.3.2 Radiological Screening

In addition to ensuring compliance with the laboratory's license and verifying estimates of radionuclide activity (Section 11.3.1), the radiological screening of packages during sample receipt serves to identify and prevent the spread of external contamination. All packages containing samples for analysis received by the laboratory should be screened for external contamination and surface exposure rate. Exceptions may include known materials (types under exclusion should be listed in the laboratory SOP) intended for analysis as: a) well-characterized samples; b) bioassays; and c) radon and associated decay products in charcoal media. Screening of packages and sample containers received in the laboratory should be conducted in accordance with the laboratory's established, documented procedures and the laboratory radiation protection and health and safety plan. The exterior of the package is screened first; if there is no evidence of contamination or that the laboratory licence would be exceeded, the package is opened up and the sample containers screened individually. These procedures should include the action level and appropriate action as established by the facility. Personnel performing screening procedures should be proficient in the use of portable radiation screening instruments and knowledgeable in radiological contamination control procedures. Health and safety considerations are affected by the suspected or known concentrations of radionuclides in a sample or the total activity of a sample.

Radiation screening is normally conducted using Geiger-Mueller (GM) detectors, ionization chambers, micro-R meters, or alpha scintillation probes, as appropriate. The laboratory should refer to any information they obtained before receipt of samples or with the samples, especially concerning the identity and concentration of radioactive and chemical constituents in the samples. Radiological screening needs to be performed as soon as practical after receipt of the package, but not later than three hours (10 CFR 20.1906) after the package is received at the licensee's facility for packages received during normal working hours. For packages received

outside of normal working hours, the screening must be performed no later than three hours from the beginning of the next workday.

Monitor the exterior of a labeled package for radioactive contamination (10 CFR 20.1906). If the package is small (less than 100 cm^2), the whole package should be wiped. Wipes are not always used, but if there is reason to believe that something has leaked, then wipes should be used. An external exposure rate determination of the package is also required within three hours after the package is received (or three hours from beginning of the next business day for packages received outside of normal working hours). This screening is performed to detect possible violations of Department of Transportation (DOT) packaging and labeling regulations, as well as to determine the possible presence of gamma- and some beta-emitting radionuclides that may require special handling. Also, screening can help to avoid introducing a high-activity sample into a low-activity area.

The Consolidated Guidance About Materials Licenses (NRC 1998b) gives the following sample model for opening packages containing radioactive material:

- Wear gloves to prevent hand contamination.
- Visually inspect the package for any sign of damage (e.g. crushed, punctured). If damage is noted, stop and notify the RSO.
- Check DOT White I, Yellow II, or Yellow III label or packing slip for activity of contents, so shipment does not exceed license possession limits.
- Monitor the external surfaces of a labeled package according to specifications in Table 8.4, Section 13.14, Item 10.
- Open the outer package (following supplier's directions if provided) and remove packing slip. Open inner package to verify contents (compare requisition, packing slip and label on the bottle or other container). Check integrity of the final source container (e.g., inspecting for breakage of seals or vials, loss of liquid, discoloration of packaging material, high count rate on smear). Again check that the shipment does not exceed license possession limits. If you find anything other than expected, stop and notify the RSO.
- Survey the packing material and packages for contamination before discarding. If contamination is found, treat as radioactive waste. If no contamination is found, obliterate the radiation labels prior to discarding in the regular trash.

- Maintain records of receipt, package survey, and wipe test results.

- Notify the final carrier and by telephone, telegram, mailgram, or facsimile, the Administrator of the appropriate NRC Regional Office listed in 10 CFR 20, Appendix D when removable radioactive surface contamination exceeds the limits of 10 CFR 71.87(i); or external radiation levels exceed the limits of 10 CFR 71.47.

11.3.3 Corrective Action

The laboratory's SOPs should specify corrective actions for routine and non-routine sample problems, including deficiency in sample volume, leaking samples, and labeling errors. The appropriate corrective action may require consulting the Project Manager and other laboratory personnel. Timely response can allow for a broader range of options and minimize the impact of the sample problem on the project. The laboratory should document the problem, the cause (if known), the corrective action taken, and the resolution of each problem that requires corrective action. The documentation should be included in the project files.

11.4 Sample Inspection

After sample receipt, the next steps are to confirm that the correct sample has been sent, to check that the appropriate field preservation and processing have been performed, and to identify any hazardous chemicals.

Documents accompanying the samples should be reviewed upon receipt of the samples at the laboratory. If the proper paperwork is not present, the Project Manager should be notified. Data recorded on the paperwork, such as collection dates, sample descriptions, requested analyses, and field staff personnel, should be compared to data on the sample containers and other documentation. Any deficiencies or discrepancies should be recorded by the laboratory and reported to the Project Manager. The documents can provide data useful for health and safety screening, tracking, and handling/processing of critical short-lived radionuclides.

11.4.1 Physical Integrity of Package and Sample Containers

This section discusses checking for leakage or breakage and tampering of packages and sample containers. Sample containers should be thoroughly inspected for evidence of sample leakage. Leakage can result from a loose lid, sample container puncture, or container breakage. Packages suspected to contain leaking sample containers should be placed in plastic bags. The authorized

user or alternate authorized user must be notified immediately for assistance. If leakage has occurred, appropriate radiological and chemical contamination controls should be implemented. Sample materials that have leaked or spilled are normally not suitable for analysis and should be properly disposed. In all cases, the laboratory's management and Project Manager should be notified of leaks, breakage, spills, and the condition of sample materials that remain in the original containers.

Containers that have leaked from a loose lid or puncture may still hold enough sample for the requested analyses. The laboratory must first determine if there is sufficient sample and if this material is representative of the original sample. An assessment should be made to determine the quantity of sample that remains and if this material is likely to be contaminated. If the sample was contaminated with the analyte of interest at the time when the container leaked, the sample is normally not analyzed. Unless appropriate information is provided in the project plan or SOW, the Project Manager should determine whether or not the sample materials can be used for analysis or if new samples are required to replace those lost due to leakage or contamination.

Packages, cooler chests, or individual sample containers may arrive at the laboratory bearing custody seals. These seals provide a means to detect unauthorized tampering. When packages or samples arrive with custody seals, they should be closely inspected for evidence of tampering. Custody seals are made from material that cannot be removed without tearing. If a custody seal is torn or absent, sample tampering may have occurred. This evidence of possible tampering is generally sufficient to preclude use of the sample for laboratory analyses. The Project Manager should be notified of the condition of the custody seal to determine if new samples are needed. Observations regarding the condition of the custody seals should be recorded according to the laboratory's standard procedures.

11.4.2 Sample Identity Confirmation

Visual inspection is the means to confirm that the correct sample has been received. Verifying the identity of a sample is a simple process where the appearance, sample container label, and chain-of-custody record or shipping manifest are compared. If all three sources of information identify the same sample, then the sample is ready for the next step. If the sample label indicates the sample is a liquid and the container is full of soil, this discrepancy would indicate a nonconformance. If the sample label states that there is 1,000 mL of liquid and there only appears to be 200 mL in the container, there may be a nonconformance. Visual inspection can be used to:

- Verify identity of samples by matching container label IDs and sample manifest IDs;

- Verify that the samples are as described by matrix and quantity;
- Check the tamper seal (if used);
- Verify field preparation (for example, filtering, removing extraneous material), if indicated; and
- Note any changes to samples since shipping, such as a reaction with the preservative.

11.4.3 Confirmation of Field Preservation

For those liquid samples requiring acid preservation, pH measurements may be performed on all or selected representative liquid samples to determine if acid has been added as a preservative. The temperature of the sample may also be part of field preservation and the actual measured temperature should be compared to the specified requirements in the documentation.

11.4.4 Presence of Hazardous Materials

The presence of hazardous materials in a sample typically creates the need for additional health and safety precautions when handling, preparing, analyzing, and disposing samples. If there is documentation on the presence of non-radiological hazardous constituents, the Project Manager should notify the laboratory about the presence of these chemicals. These chemical contaminants should be evaluated by the laboratory to determine the need for special precautions. The laboratory can also perform preliminary sample screening for chemical contaminants using screening devices such as a photoionization detector for volatile components. The presence of suspected or known hazardous materials in a sample should be identified, if possible, during project planning and documented in the plan document and SOW. Visual inspection can also be used such as checking the color of the sample (i.e., a green-colored water sample may indicate the presence of high chromium levels). The presence of suspected or known hazardous materials determined in the field should be communicated to the laboratory prior to the arrival of samples and noted on documentation accompanying the samples to the laboratory. If no documentation on non-radiological hazardous constituents is available, the laboratory should review previous experience concerning samples from the site to assess the likelihood of receiving samples with chemical contaminants. The laboratory should notify the Health and Safety Officer and the Project Manager about the presence of potentially hazardous chemical contaminants.

11.4.5 Corrective Action

Visual inspection can also verify whether field sample preparation was performed as stated in accompanying documentation. Samples that were not filtered in the field or that reacted with the preservative to form a precipitate may represent a significant problem to the laboratory. If it appears that the sample was filtered in the field (i.e., there is a corresponding filter sample for the liquid sample), the liquid generally will be analyzed as originally specified. Laboratory personnel should check the project plan or SOW to see if the filter and filtered materials require analyses along with the filtered sample. If it appears that the sample was not filtered in the field (i.e., there is no corresponding filter, there are obviously solid particles in a liquid sample), sample documentation should be reviewed to determine if a deviation from the project plan was documented for the sample. It may be appropriate to filter the sample in the laboratory. The Project Manager should be notified immediately to discuss possible options such as filtering the sample at the laboratory or collecting additional samples.

One example of a corrective action for inspection is, if the pH is out of conformance, it may be possible to obtain a new sample. If it is not possible or practical to obtain a new sample, it may be possible to acidify the sample in the laboratory.

Visual inspection can serve to check certain aspects of sample collection. For example, if the SOP states that a soil sample is supposed to have twigs, grass, leaves, and stones larger than a certain size removed during sample collection and some of this foreign material is still included as part of the sample, this discrepancy results in a nonconformance.

11.5 Laboratory Sample Tracking

Sample tracking should be done to ensure that analytical results are reported for the "correct" sample. A good sample tracking system helps to prevent sample mix-up. Sample tracking is a process by which the location and status of a sample can be identified and documented. The laboratory is responsible for sample tracking starting with receipt (at which time a unique laboratory tracking number is assigned), during sample preparation, and after the performance of analytical procedures until final sample disposition. The process of sample tracking begins the moment a field worker assigns an identification number (based on the information provided in the appropriate plan document) and documents how materials are collected. The way samples are transported from the field to the laboratory should be documented. The sample receiving procedures and documentation should be consistent when applicable with 10 CFR Part 20 Subpart J, and the client's requirements as stated in the appropriate plan document or statement of work.

11.5.1 Sample Log-In

Laboratory sample numbers should be assigned to each sample in accordance with the laboratory's SOP on sample codes. Each sample should receive a unique tracking number by which it can be logged into the laboratory tracking system, scheduled for analysis, tracked, and disposed. Information to be recorded during sample log-in should include the field sample identification number, laboratory sample tracking number, date and time samples were collected and received, reference date for decay calculations, method of shipment, shipping numbers, condition of samples, requested analyses, number and type of each sample, quality control requirements, special instructions, and other information relevant to the analyzing and tracking of samples at the laboratory. Laboratory sample tracking is a continuation of field sample tracking.

Documents generated for laboratory sample tracking must be sufficient to verify the sample identity, that the sample may be reliably located, and that the right sample is analyzed for the right analyte. The documentation should include sample log-in records, the analysis request form, names of staff responsible for the work, when procedures are completed, and details concerning sample disposal. The documentation must conform to the laboratory's SOPs.

During sample log-in, laboratory quality control (QC) samples may be scheduled for the analyses requested. The type and frequency of QC samples should be provided by the plan document or SOW and consistent with the laboratory's SOPs.

11.5.2 Sample Tracking During Analyses

At this point, samples are introduced into the laboratory's analytical processing system. The information gathered during screening, along with the assigned tracking identification, passes to the laboratory where specific preparation and analyses are performed. The sample may be further sub-sampled. Each sub-sample, along with the original sample, requires tracking to account for all materials handled and processed in the laboratory.

At the same time that samples are received at the laboratory, each set of samples should be accompanied by documents listing requests for specific analyses. This documentation should be compared to separate paperwork obtained before sample receipt. Laboratory management personnel should be notified of any discrepancies. The requested analyses should be entered into the laboratory's tracking system. Typically, only one sample container of sufficient volume or quantity will be provided for a single or multiple set of different analyses. Each aliquant removed from the original container may require tracking (and perhaps a different tracking number).

Aliquants used during the analytical process can be tracked using analysis laboratory notebooks, forms, or bench sheets that record laboratory tracking numbers, analyte, reference date for decay correction, aliquant size, and designated quality control samples. Bench sheets are loose-leaf or bound pages used to record information during laboratory work. Bench sheets are used to assist in sample tracking. Each sheet is helpful for identifying and processing samples in batches that include designated quality control samples. The bench sheet, along with the laboratory log book, can later be used to record analytical information for use during the data review process. Bench sheets can also be used to indicate that sample aliquants were in the custody of authorized personnel during the analytical process.

After receipt, verification of sample information and requested analyses, and assignment of laboratory sample tracking numbers, the requested analyses can be scheduled for performance in accordance with laboratory procedures. Using this system, the laboratory can formulate a work schedule, and completion dates can be projected.

11.5.3 Storage of Samples

If samples are to be stored and analyzed at a later date, they must be placed in a secure area that meets all custody requirements. Before storage, any special preservation requirements, such as refrigeration or additives, should be determined.

The laboratory should keep records of the sample identities and the location of the sample containers. Unused sample aliquants should be returned to the storage area for final disposition. In addition, for some samples, depending on the level of radioactivity or hazardous constituents present, the laboratory must record when the sample was disposed and the location of the disposal facility. These records are necessary to ensure compliance with the laboratory's license for radioactive materials and other environmental regulations.

Areas where samples are stored must be designated and posted as radioactive materials storage areas. Depending on the activity level of the samples, storage areas may require special posting. If additional storage space or shielding is needed, arrangements that are consistent with the license must be made with the authorized user. See Chapter 20 on waste disposal for more information.

11.6 References

American Society of Testing and Materials (ASTM) D4840. Standard Guide for *Sampling Chain-of-Custody Procedures*.

American Society of Testing and Materials (ASTM) D5172. Standard Guide for *Documenting the Standard Operating Procedures Used for the Analysis of Water.*

U.S. Environmental Protection Agency (EPA). 1985. *NEIC Policies and Procedures.* EPA-300/9-78DDI-R, June.

U.S. Environmental Protection Agency (EPA). 1995. QA/G-6, *Guidance for the Preparation of Standard Operating Procedures (SOPS) for Quality-Related Documents.*

U.S. Nuclear Regulatory Commission. 1998b. *Consolidated Guidance About Materials Licenses,* Volume 7. (NRC91). NUREG 1556.

12 LABORATORY SAMPLE PREPARATION

12.1 Introduction

On first impression, sample preparation may seem the most mundane aspect of an analytical protocol. However, it is critical that the analyst realize and remember that a determination is only as good as the sample preparation that has preceded it. If an aliquant taken for analysis does not represent the original sample accurately, the results of this analysis are questionable. As a general rule, the error in sampling and the sample preparation portion of an analytical procedure is considerably higher than that in the methodology itself, as illustrated in Figure 12.1.

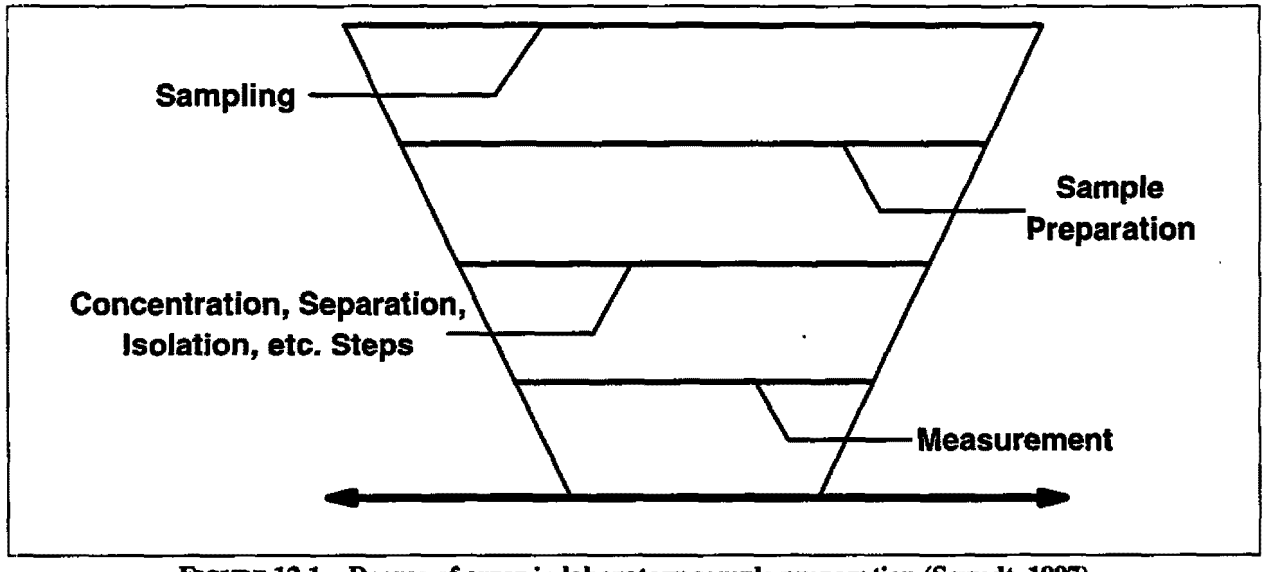

FIGURE 12.1—Degree of error in laboratory sample preparation (Scwedt, 1997)

One goal of laboratory sample preparation is to provide, without sample loss, representative aliquants that are free of laboratory contamination that will be used in the next steps of the protocol. Samples are prepared in accordance with applicable standard operating procedures (SOPs) and laboratory SOPs using information provided by field sample preparation (Chapter 10, *Field and Sampling Issues that Affect Laboratory Measurements*), sample screening activities, and objectives given in the appropriate planning documents. *The laboratory sample preparation techniques presented in this chapter include the physical manipulation of the sample (heating, screening, grinding, mixing, etc.) up to the point of dissolution. Steps such as adding carriers and tracers, followed by wet ashing or fusion, are discussed in Chapter 13 (Sample Dissolution) and Chapter 14 (Separation Techniques).*

This chapter presents some general guidance for sample preparation on the avoidance of sample loss and of sample contamination. Owing to the physical nature of the media, sample preparation for solids requires the most attention, and therefore is discussed at great length (Section 12.3). General procedures for preparing solid samples (such as drying, obtaining a constant weight, grinding, sieving, mixing, and subsampling) are discussed. Some sample preparation procedures then are presented for typical types of solid samples (e.g., soil and sediment, biota, vegetation including food, etc.). This chapter concludes with specific guidance for preparing samples of filters (Section 12.4), wipes (Section 12.5), liquids (Section 12.6), gases (Section 12.7), and bioassay (Section 12.8).

12.2 General Guidance for Sample Preparation

Some general considerations during sample preparation are to minimize sample losses and to prevent contamination. Possible mechanisms for sample loss during preparation steps are discussed in Section 12.2.1, and the contamination of samples from sources in the laboratory is discussed in Section 12.2.2. Control of contamination through cleaning labware is important and described in Section 12.2.3, and laboratory contamination control is discussed in Section 12.2.4.

12.2.1 Potential Sample Losses During Preparation

Materials may be lost from a sample during laboratory preparation. The following sections discuss the potential types of losses and the methods used to control them. The addition of tracers or carriers (Chapter 13) is encouraged at the earliest possible point and prior to any sample preparation step where there might be a loss of analyte. Such preparation steps may include homogenization or sample heating. The addition of tracers or carriers prior to these steps helps to account for any analyte loss during sample preparation.

12.2.1.1 Losses as Dust or Particulates

When a sample is dry ashed, a fine residue (ash) is often formed. The small particles in the residue are resuspended readily by any flow of air over the sample. Air flows are generated by changes in temperature (e.g., opening the furnace while it is hot) or by passing a stream of gas over the sample during heating to assist in combustion. These losses are minimized by ashing samples at as low a temperature as possible, gradually increasing and decreasing the temperature during the ashing process, using a slow gas-flow rate, and never opening the door of a hot furnace (Section 12.3.1). If single samples are heated in a tube furnace with a flow of gas over the sample, a plug of glass or quartz wool can be used to collect particulates or an absorption

vessel can be used to collect volatile materials. At a minimum, all ash or finely ground samples should be covered before they are moved.

Solid samples are often ground to a fine particle size before they are fused or wet ashed (see Chapters 13 and 14 on dissolution and separation) to increase the surface area and speed up the reaction between the sample and the fluxing agent or acid. Since solid samples are frequently heterogeneous, a source of error arises from the difference in hardness among the sample components. The softer materials are converted to smaller particles more rapidly than the harder ones, and therefore, any loss in the form of dust during the grinding process will alter the composition of the sample. The finely ground particles are also susceptible to resuspension. Samples may be moistened carefully with a small amount of water before adding other reagents. Reagents should be added slowly to prevent losses as spray owing to reactions between the sample and the reagents.

12.2.1.2 Losses Through Volatilization

Some radionuclides are volatile under specific conditions (e.g., heat, grinding, strong oxidizers), and care should be taken to identify samples requiring analysis for these radionuclides. Special preparation procedures should be used to prevent the volatilization of the radionuclide of interest.

The loss of volatile elements during heating is minimized by heating without exceeding the boiling point of the volatile compound. Ashing aids can reduce losses by converting the sample into less volatile compounds. These reduce losses but can contaminate samples. During the wet ashing process, losses of volatile elements can be minimized by using a reflux condenser. If the solution needs to be evaporated, the reflux solution can be collected separately. Volatilization losses can be prevented when reactions are carried out in a sealed tube or a closed metal or Teflon™ bomb. Table 12.1 lists some commonly analyzed radioisotopes, their volatile chemical form, and the boiling point of that species at standard pressure (note that the boiling point may vary based on solution, matrix, etc.).

Often the moisture content, and thus, the chemical composition of a solid is altered during grinding and crushing (Dean, 1995). Decreases in water content are sometimes observed while grinding solids containing essential water in the form of hydrates, likely as a result of localized heating. (See Section 12.3.1.2 for a discussion of the types of moisture present in solid samples.) Moisture loss is also observed when samples containing occluded water are ground and crushed. The process ruptures some of the cavities, and exposes the water to evaporation. More commonly, the grinding process results in an increase in moisture content owing to an increase in

surface area available for absorption of atmospheric water. Both of these conditions will affect the analysis of ^{3}H since ^{3}H is normally present in environmental samples as ^{3}HOH.

TABLE 12.1 — Examples of Volatile Radionuclides

Isotope	Chemical Form	Boiling Point (°C)
Tritium — ^{3}H	H_2O	100
Carbon — ^{14}C	CO_2 (produced from CO_3^{-2} or oxidation of organic material)	-78.5
Iodine — ^{131}I, ^{129}I	I_2	185.2 (sublimes readily)
Cesium — ^{134}Cs, ^{135}Cs, ^{137}Cs	Cs metal Cs oxides (nitrates decompose to oxides) CsCl	678.4 ~650 1290
Ruthenium — ^{106}Ru	RuO_4 $RuCl_3 \cdot xH_2O$	40 decomposes above 500
Technetium — ^{99}Tc	Tc_2O_7 $TcCl_4$	310.6 Sublimes above 300

Source: Greenwood and Earnshaw (1984).

Additional elements that volatilize under specific conditions include arsenic, antimony, tin, polonium, lead, selenium, mercury, germanium, and boron. Osmium is volatilized as the tetroxide under oxidizing conditions similar to those for ruthenium. Carbon, phosphorus, and silicon may be volatilized as hydrides, and chromium is volatilized under oxidizing conditions in the presence of chloride.

12.2.1.3 Losses Owing to Reactions Between Sample and Container

Specific elements may be lost from sample materials owing to interaction with a container. Such losses may be significant, especially for trace analyses used in radioanalytical work. Adsorption reactions are discussed in Chapter 10 for glass and plastic containers. Losses owing to adsorption may be minimized by using pretreated glassware with an established hydrated layer. Soaking new glassware overnight in a dilute nitric or hydrochloric acid solution will provide an adequate hydrated layer. Glassware that is used on a regular basis will already have established an adequate hydrated layer. The use of strong acids to maintain a pH less than one also helps minimize losses from adsorption.

Reactions among analytes and other types of containers are described in Table 12.2. Leaving platinum crucibles uncovered during dry ashing to heat samples will minimize reduction of samples to base metals which form alloys with platinum. It is recommended that porcelain not be used for analysis of lead, uranium, and thorium because the oxides of these elements react with porcelain glazes. Increasing the amount of sample for dry ashing increases the amount of ash, allowing trace elements to react with the ash instead of with the container.

TABLE 12.2 — Properties of Sample Container Materials

Material	Recommended Use	Properties
Borosilicate Glass	General applications	Transparent; good thermal properties; fragile; attacked by HF, H_3PO_4, and alkaline solutions.
Fused Quartz	High temperature applications	Transparent; excellent thermal properties (up to 1100° C); fragile; more expensive than glass; attacked by HF, H_3PO_4, and alkaline solutions.
Porcelain	High temperature applications	Used at temperatures up to 1100° C; less expensive than quartz; difficult to shape; attacked by HF, H_3PO_4, and alkaline solutions.
Platinum	High temperature or corrosive applications	Virtually unaffected by acids, including HF; dissolves readily in mixtures of HNO_3 and HCl, Cl_2 water or Br_2 water; adequate resistance to H_3PO_4; very expensive; forms alloys with Hg, Pb, Sn, Au, Cu, Si, Zn, Cd, As, Al, Bi, and Fe, which may be formed under reducing conditions; permeable to H_2 at red heat, which serves as a reducing agent; may react with S, Se, Te, P, As, Sb, B, and C to damage container; soft and easily deformed, often alloyed with Ir, Au, or Rh for strength. Do not use with Na_2CO_3 for fusion.
Nickel	Molten alkali metal hydroxide and na_2o_2 fusions	Suitable for use with strongly alkaline solutions.
Zirconium	Peroxide fusions	Less expensive alternative to platinum; extremely resistant to HCl; resistant to HNO_3; resistant to 50% H_2SO_4 and 60% H_3PO_4 up to 100° C; resistant to molten NaOH; attacked by molten nitrate and bisulfate; usually available as Zircaloy—98% Zr, 1.5% Sn, trace Fe, Cr, and Ni.
Alumina (Al_2O_3)	Acids and alkali melts at low temperatures	Resistant to acids and alkali melts; rapidly attacked by bisulfate melts; brittle, requires thick walled containers.
Polyethylene	Sample and reagent storage	Resistant to many acids; attacked by 16M HNO_3 and glacial acetic acid; begins to soften and lose shape at 60° C; appreciably porous to Br_2, NH_3, H_2S, H_2O, and HNO_3 (aqueous solutions can lose ~1% volume per year when stored for extended periods of time).
Teflon™	Corrosive applications	Inert to almost all inorganic and organic compounds except F_2; porosity to gases is significantly less than that of polyethylene; safe to use at 250° C but decomposes at 300° C; difficulty in shaping containers results in high cost; low thermal conductivity (requires long periods of time to heat samples).

12.2.2 Contamination from Sources in the Laboratory

Contamination leads to biased data that misrepresent the concentration or presence of radionuclides in a specific sample. Therefore, laboratory personnel should take appropriate measures to prevent the contamination of samples. Such precautions are most important when multiple samples are processed together. Possible sources of contamination include:

- Airborne;
- Reagents (tracers are discussed in Chapter 13);
- Glassware/equipment; and
- Facilities.

The laboratory should use techniques that eliminate air particulates or the introduction of any outside material (such as leaks from aerosols) into samples and that safeguard against using contaminated glassware or laboratory equipment. Contamination of samples can be controlled by adhering to established procedures for equipment preparation and decontamination before and after each sample is prepared. Additionally, the results of blank samples (e.g., sand), which are run as part of the internal quality assurance program, should be closely monitored, particularly following the processing of samples with elevated activity.

"Cross-contamination" is the contamination of one sample by another sample that is being processed concurrently or that was processed prior to the current sample leaving a residue on the equipment being used. Simply keeping samples covered whenever practical is one technique to minimize cross-contamination. Another technique is to order the processing of samples beginning with the lowest contamination samples first. It is not always possible to know the exact rank of samples, but historical or field screening data may be useful.

Laboratory personnel should be wary of using the same equipment (gloves, tweezers for filters, contamination control mats, etc.) for multiple samples. Countertops and other preparation areas should be routinely monitored for contamination.

12.2.2.1 Airborne Contamination

Airborne contamination is most likely to occur when grinding or pulverizing solid samples. Very small particles (~10 microns) may be produced, suspended in air, and transported in the air before settling onto a surface. Other sources of potential airborne contamination include samples that already consist of very small particles, or radionuclides that decay through a gaseous intermediate (i.e., ^{226}Ra decays to ^{222}Rn gas and eventually decays to ^{210}Pb). Therefore, the

158 grinding or pulverizing of solid samples or the handling of samples that could produce airborne
159 contamination should be carried out under a laboratory hood to prevent dispersal or deposition in
160 the laboratory of contaminated air particulates. These particles easily can contaminate other
161 samples stored in the area. To prevent such cross-contamination, other samples should be
162 covered or removed from the area while potential sources of airborne contamination are being
163 processed.

164 If contamination from the ambient progeny of ^{222}Rn is a concern, this can be avoided by
165 refraining from the use of suction filtration in chemical procedures, prefiltering of room air
166 (Lucas, 1967), and use of radon traps (Lucas, 1963; Sedlet, 1966). The laboratory may have
167 background levels of radon progeny from its construction materials.

168 12.2.2.2 Contamination of Reagents

169 Contamination from radiochemical impurities in reagents is especially troublesome in low-level
170 work (Wang et al., 1975). Care must be taken in obtaining reagents with the lowest contamina-
171 tion possible. Owing to the ubiquitous nature of uranium and thorium, they and their progeny are
172 frequently encountered in analytical reagents. For example, Yamamoto et al. (1989) found
173 significant ^{226}Ra contamination in common barium and calcium reagents. Other problematic
174 reagents include the rare earths (especially cerium salts), cesium salts which may contain ^{40}K or
175 ^{87}Rb, and potassium salts. Precipitating agents such as tetraphenyl borates and chloroplatinates
176 may also suffer from contamination problems. In certain chemical procedures, it is necessary to
177 replace inert carriers of the element of interest with non-isotopic carriers when it is difficult to
178 obtain the inert carrier in a contamination-free condition. Devoe (1961) has written an extensive
179 review article on the radiochemical contamination of analytical reagents.

180 12.2.2.3 Contamination of Glassware/Equipment

181 Other general considerations in sample preparation include the cleaning of glassware and
182 equipment (Section 12.2.3). Criteria established in the planning documents or laboratory SOPs
183 should give guidance on proper care of glassware and equipment (i.e., scratched glassware
184 increases the likelihood of sample contamination and losses owing to larger surface area).
185 Glassware should be routinely inspected for scratches, cracks, etc., and discarded if damaged.
186 Blanks and screening should be used to monitor for contamination of glassware.

187 Whenever possible, the use of new or disposable containers or labware is recommended. For
188 example, disposable weigh boats can be used to prevent contamination of a balance. Disposable
189 plastic centrifuge tubes are often less expensive to use than glass tubes that require cleaning after

every use. If non-disposable containers or labware are used, it may be necessary to use new materials for each new project to reduce the potential for contamination. Blanks can be used to detect cross-contamination. Periodic rinsing with a dilute solution of nitric acid can aid in maintaining clean glassware. However, Bernabee et al. (1980) could not easily remove nuclides sorbed onto the walls of plastic containers by washing with strong mineral acids. They report that nuclides can be wiped from the walls, showing the importance of the physical action of a brush to the cleaning process.

12.2.2.4 Contamination of Facilities

In order to avoid contamination of laboratory facilities and possible contamination of samples or personnel, good laboratory practices must be constantly followed and the laboratory must be kept in clean condition. The laboratory should establish and maintain a Laboratory Contamination Control Program (Section 12.2.4) to avoid contamination of facilities and to deal with it expeditiously if it occurs.

12.2.3 Cleaning of Labware, Glassware, and Equipment

12.2.3.1 Labware and Glassware

Some labware is too expensive to be used only once (e.g., crucibles, Teflon™ beakers, separatory funnels). Labware that will be used for more than one sample should be subjected to thorough cleaning between uses. A typical cleaning protocol includes a detergent wash, an acid soak (HCl, HNO_3, or citric acid), and a rinse with deionized or distilled water. As noted in Chapter 10, the use of a brush to physically scrub glassware aids in the removal of contaminates.

The *Chemical Technician's Ready Reference Handbook* (Shugar and Ballinger, 1996) offers practical advice on washing and cleaning laboratory glassware:

- Always clean your apparatus immediately after use. It is much easier to clean the glassware before the residues become dry and hard. If dirty glassware cannot be washed immediately, it should be left in water to soak.

- Thoroughly rinse all soap or other cleaning agent residue after washing glassware to prevent possible contamination. If the surface is clean, the water will wet the surface uniformly; if the glassware is still soiled, the water will stand in droplets.

- Use brushes carefully and be certain that the brush has no exposed sharp metal points that can scratch the glass. Scratched glassware increases the likelihood of sample contamination and losses owing to larger surface areas. Moreover, scratched glassware is more easily broken, especially when heated.

Automatic laboratory dishwashers and ultrasound or ultrasonic cleaners are also used in many radiochemical laboratories. It is important to note that cleaning labware in an automatic laboratory dishwasher alone may not provide adequate decontamination. Contaminated glassware may need to be soaked in acid or detergent to ensure complete decontamination. Ultrasonic cleaning in an immersion tank is an exceptionally thorough process that rapidly and efficiently cleans the external, as well as the internal, surfaces of glassware or equipment. Ultrasonic cleaners generate high-frequency sound waves and work on the principle of "cavitation," the formation and collapse of submicron bubbles. These bubbles form and collapse about 25,000 times each second with a violent microscopic intensity which produces a scrubbing action (Shugar and Ballinger, 1996). This action effectively treats every surface of the labware because it is immersed in the solution and the sound energy penetrates wherever the solution reaches.

The *Manual for the Certification of Laboratories Analyzing Drinking Water* (EPA, 1992) contains a table of glassware cleaning and drying procedures for the various methods given in the manual (including methods for the analysis of radionuclides in water). The suggested procedure for cleaning glassware for metals analysis is to wash with detergent, rinse with tap water, soak for 4 hours in 20 percent (v/v) HNO_3 or dilute HNO_3 (8 percent)/HCl (17 percent), rinse with reagent water, then air dry. Shugar and Ballinger (1996) suggest treating acid-washed glassware by soaking it in a solution containing 2 percent NaOH and 1 percent disodium ethylenediamine tetraacetate for 2 hours, followed by a number of rinses with distilled water to remove metal contaminants.

More specifically to radionuclides, in their paper discussing the simultaneous determination of alpha-emitting nuclides in soil, Sill et al. (1974) examined the decontamination of certain radionuclides from common labware and glassware:

> By far the most serious source of contamination is the cell, electrode, and "O" ring used in the electrodeposition step. Brief rinsing with a strong solution of hydrochloric acid containing hydrofluoric acid and peroxide at room temperature was totally ineffective in producing adequate decontamination. Boiling anode and cell with concentrated nitric acid for 10 to 15 minutes removed virtually all of the activity resulting from the analysis of samples containing less than 500 disintegrations per minute (dpm). When larger quantities of activity such as the 2.5×10^4 counts per minute (cpm) used in the material

> studies ... had been used, a second boiling with clean acid was generally required. However, boiling nitric acid precipitates polonium and other procedures have to be used in its presence. When such high levels of activity have been used, a blank should be run to ensure that decontamination was adequate before the system is permitted to be used in the analysis of subsequent low-level samples. Prudence suggests that a separate system should be reserved for low-level samples and good management exercised over the level of samples permitted in the low-level system to minimize the number of blanks and full-length counting times required to determine adequate decontamination.
>
> ...Beakers, flasks, and centrifuge tubes in which barium sulfate has been precipitated must be cleaned by some agent known to dissolve barium sulfate, such as boiling perchloric or sulfuric acids or boiling alkaline DTPA [diethylenetriaminepentacetate]. This is a particularly important potential source of contamination, particularly if hot solutions containing freshly-precipitated barium sulfate are allowed to cool without stirring. Some barium sulfate post-precipitates after cooling and adheres to the walls so tenaciously that chemical removal is required. Obviously, the barium sulfate will contain whichever actinide is present, and will not dissolve even in solutions containing hydrofluoric acid. Beakers or flasks in which radionuclides have been evaporated to dryness will invariably contain residual activity which generally requires a pyrosulfate fusion to clean completely and reliably. Separatory funnels can generally be cleaned adequately by rinsing them with ethanol and water to remove the organic solvent, and then with hydrochloric-hydrofluoric acids and water to remove traces of hydrolyzed radionuclides...

However, one should note that current laboratory safety guidelines discourage the use of perchloric acid (Schilt, 1979).

12.2.3.2 Equipment

In order to avoid cross-contamination, grinders, sieves, mixers and other equipment should be cleaned before using them for a new sample. Cleaning equipment prior to use is only necessary if the equipment has not been used for some time. The procedure can be as simple or as complicated as the analytical objectives warrant as illustrated by Obenhauf et al. (website reference) in the *SPEX Certiprep Handbook of Sample Preparation and Handling*. In some applications, simply wiping down the equipment with ethanol may suffice. Another practical approach is to brush out the container, and briefly process an expendable portion of the next sample and discard it. For more thorough cleaning, one may process one or more batches of pure quartz sand through the piece of solid processing equipment, and then wash it carefully. The

efficacy of the decontamination is determined by monitoring this sand for radionuclide contamination.

An effective cleaning procedure for most grinding containers is to grind pure quartz sand together with hot water and detergent, then to rinse and dry the container. This approach incorporates a safety advantage in that it controls respirable airborne dusts. It is important to note that grinding containers become more difficult to clean with age because of progressive pitting and scratching of the grinding surface. Hardened steel containers can also rust, and therefore should be dried thoroughly after cleaning and stored in a plastic bag containing a desiccating agent. If rust does occur, the iron oxide coating can be removed by a warm dilute oxalic acid solution or by abrasive cleaning.

12.2.4 Laboratory Contamination Control Program

The laboratory should establish a general program to prevent the contamination of samples. Included in the program should be ways to detect contamination from any source during the sample preparation steps if contamination of samples occurs. The laboratory contamination control program should also provide the means to correct procedures to eliminate or reduce any source of contamination. Some general aspects of a control program include:

- Appropriate engineering controls, such as ventilation, shielding, etc., should be in place.
- The laboratory should be kept clean and good laboratory practices should be followed. Personnel should be well-trained in the safe handling of radioactive materials.
- Counter tops and equipment should be cleaned and decontaminated following spills of liquids or dispersal of finely powdered solids. Plastic-backed absorbent benchtop coverings or trays help to contain spills.
- There should be an active health physics program that includes frequent monitoring of facilities and personnel.
- Wastes should be stored properly and not allowed to accumulate in the laboratory working area. Satellite accumulation areas should be monitored.
- Personnel should be mindful of the use of proper personnel protection equipment and practices (e.g., habitual use of lab coats, frequent glove changes, routine hand washes).

- Operations should be segregated according to activity level. Separate equipment and facilities should be used for elevated and low-level samples whenever possible.

- SOPs describing decontamination and monitoring of labware, glassware, and equipment should be available.

- Concentrated standard stock solutions should be kept isolated from the general laboratory working areas.

As an example, Kralian et al. (1990) have published the guidelines for effective low-level contamination control.

12.3 Solid Samples

This section discusses laboratory preparation procedures for solid samples as illustrated in Figure 12.2. General procedures such as exclusion of unwanted material in the sample; drying, charring, and ashing of samples; obtaining a constant weight (if required); and homogenization are discussed first. Examples of preparative procedures for solid samples are then presented.

Solid samples may consist of a wide variety of materials, including:

- Soil and sediment;
- Biota (plants and animals); and
- Other materials (metal, concrete, asphalt, solid waste, etc.).

Before a solid sample is prepared, the specific procedures given in the planning documents should be reviewed. This review should result in a decision that indicates whether materials other than those in the intended matrix should be removed, discarded, or analyzed separately. Any material removed from the sample should be identified, weighed, and documented.

To ensure that a representative aliquant of a sample is analyzed, the sample should first be dried or ashed and then blended or ground thoroughly (Appendix F). Homogenization should result in a uniform distribution of analytes and particles throughout the sample. The size of the particles that make up the sample will have a bearing on the representativeness of each aliquant.

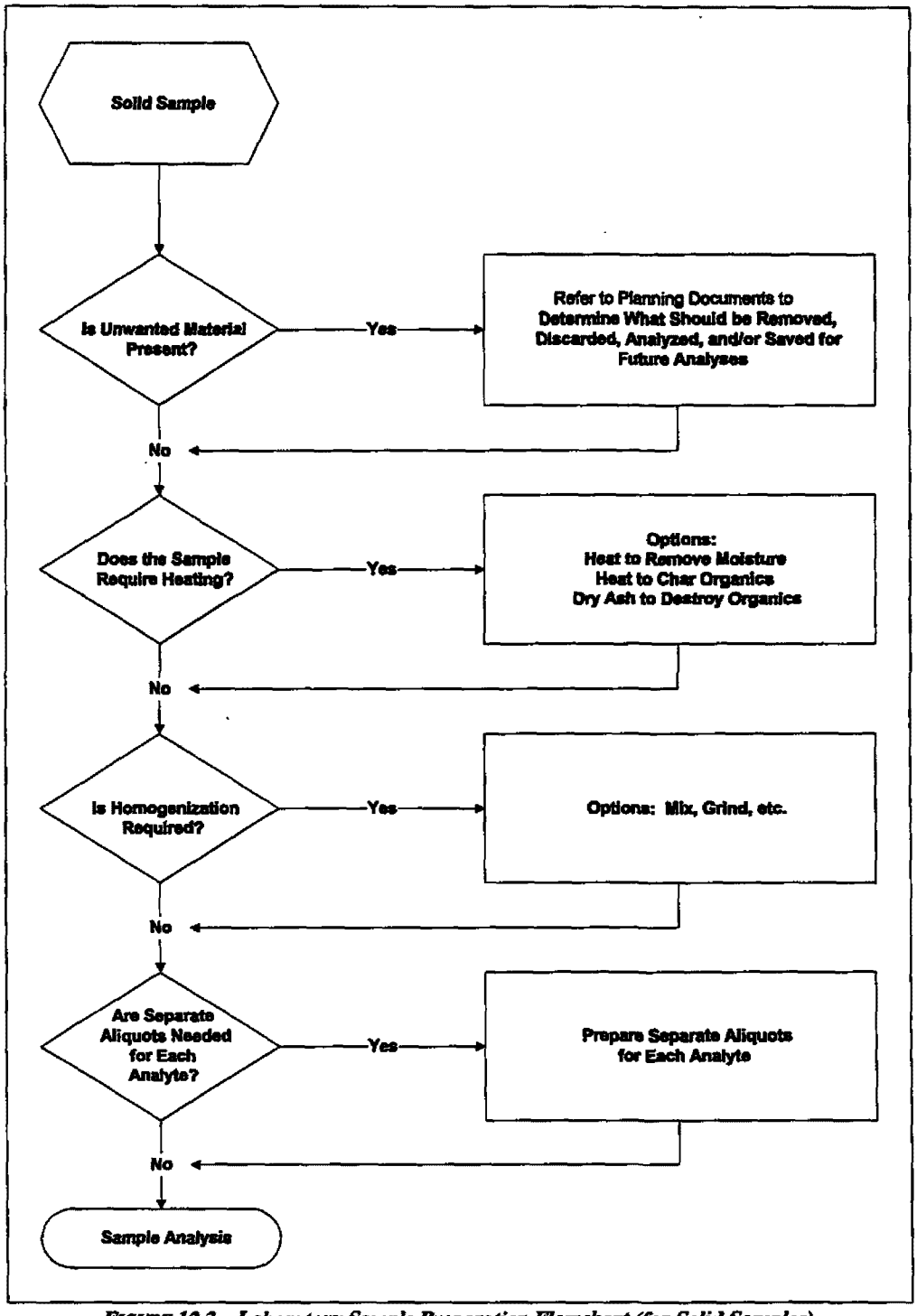

FIGURE 12.2—Laboratory Sample Preparation Flowchart (for Solid Samples)

338 ### 12.3.1 General Procedures

339 The following sections discuss the general procedures for exclusion of material, heating solid
340 samples (drying, charring, and ashing), obtaining a constant weight, mechanical manipulation
341 grinding, sieving, and mixing), and subsampling. Not every step is done for all solid sample
342 categories (soil/sediment, biota, and other) but are presented here to illustrate the steps that could
343 be taken during preparation.

344 #### 12.3.1.1 Exclusion of Material

345 *Exclusion of Material by Size and Particles.* During solid preparation, some particles may be
346 identified in the sample that are not a part of the matrix intended for analysis. Examples of such
347 particles are rocks and pebbles or fragments of glass and plastic. Depending on the specific
348 procedures given in the planning documents on the constitution of the sample taken, rocks and
349 pebbles can be removed and analyzed separately if desired. The sample should be weighed before
350 and after any material is removed. Other materials that are not a part of the required matrix can
351 also be removed and analyzed separately. If analysis of the material removed is necessary,
352 applicable SOPs should be used to prepare the material for analysis.

353 *Exclusion of Organic Material.* Leaves, twigs, and grass can easily be collected inadvertently
354 along with samples of soil or sediment. Because these are not usually intended for analysis, they
355 are often removed and stored for future analysis, if necessary. The material removed should be
356 identified, if possible, and weighed.

357 #### 12.3.1.2 Principles of Drying Techniques

358 Applying elevated temperatures during sample preparation is a widely used technique for the
359 following reasons:

360 - To remove moisture or evaporate liquids (raise the temperatures to 60° to 110° C).

361 - To prepare organic material for subsequent wet ashing or fusion ("char" the material by
362 heating to medium temperature of 200° to 300° C).

363 - To prepare the sample for subsequent determination of nonvolatile constituents (dry ash at
364 high temperature of 450° to 750° C).

Once a decision is made to use elevated temperatures during sample preparation, several questions should be considered:

- What material should be used for the sample container?
- What should serve as the heat source?
- How quickly should the temperature be raised? (Rate of stepwise temperature increase)
- What is the maximum temperature to which the sample should be exposed?
- How long should the sample be heated at the maximum temperature?
- How quickly should the sample be cooled afterward?

The following sections provide information related to these questions.

Note that there are times during sample preparation when samples should not be heated. For example, samples to be prepared for ^{3}H or ^{14}C determination should not be heated. Since ^{3}H is normally present as tritiated water in environmental samples, heating will remove the ^{3}H. Similarly, ^{14}C is usually present in environmental samples as carbonates or $^{14}CO_2$ dissolved in water, and heating will release ^{14}C as a gas. Samples to be analyzed for iodine, mercury, antimony, or other volatile elements should be heated only under conditions specified in the planning documents. If both volatile and nonvolatile elements are determined from the same sample, aliquants of the original sample should be removed for determination of the volatile elements.

Ovens, furnaces, heat lamps, and hot plates are the traditional means to achieve elevated temperatures in the laboratory. However, more recently, microwave ovens have added an additional tool for elevating temperature during sample preparation. Walter et al. (1997) and Kingston and Jassie (1988) give an overview of the diverse field of microwave-assisted sample preparation. A dynamic database of research articles related to this topic can be found at the SamplePrep Web™ at http://www.sampleprep.duq.edu/index.html. As microwave sample preparation has developed, numerous standard methods with microwave assistance have been approved by the American Society for Testing and Materials (ASTM), Association of Official Analytical Chemists (AOAC), and the U.S. Environmental Protection Agency (EPA). The majority of the microwave-assisted methods are for acid-dissolution (Chapter 13), but several are for drying samples.

Alternatives to heating samples include drying them slowly in a vacuum desiccator, air-drying, or freeze-drying. ASTM D3974 describes three methods of preparing soils, bottom sediments, suspended sediments, and waterborne materials: (1) freeze-drying; (2) air-drying at room temperature; and (3) accelerated air-drying.

Drying Samples

It must be determined at the start of an analytical procedure if the results are to be reported on an *as-received* or *dry-weight* basis. Most analytical results for solid samples should be reported on a dry-weight basis, which denotes material dried at a specified temperature to a constant weight or corrected through a "moisture" determination made on an aliquant of the sample taken at the same time as the aliquant taken for sample analysis.

Typically, samples are dried at temperatures of 105° to 110° C. Sometimes it is difficult to obtain constant weight at these temperatures, then higher temperatures must carefully be used. Alternatively, for samples that are extremely heat sensitive and decompose readily, vacuum desiccation or freeze-drying techniques are applicable.

The presence of water in a sample is a common problem frequently facing the analyst. Water may be present as a contaminant (i.e., from the atmosphere or from the solution in which the substance was formed) or be bonded as a chemical compound (i.e., a hydrate). Regardless of its origin, water plays a role in the composition of the sample. Unfortunately, especially in the case of solids, water content is variable and depends upon such things as humidity, temperature, and the state of subdivision. Therefore, the make-up of a sample may change significantly with the environment and the method of handling.

Traditionally, chemists distinguish several ways in which water is held by a solid (Dean, 1995).

- Essential water is an integral part of the molecular or crystal structure and is present in stoichiometric quantities, for example, $CaC_2O_4 \cdot 2H_2O$.

- Water of constitution is not present as such in the solid, but is formed as a product when the solid undergoes decomposition, usually as a result of heating. For example, $Ca(OH)_2 \rightarrow CaO + H_2O$.

- Nonessential water is retained by physical forces, is non-stoichiometric, and is not necessary for the characterization of the chemical composition of the sample.

- Absorbed water is retained on the surface of solids in contact with a moist environment, and therefore, is dependent upon the humidity, temperature, and surface area of the solid.

- Sorbed water is encountered with many colloidal substances such as starch, charcoal, zeolite minerals, and silica gel and may amount to as much as 20 percent or more of the solid. Sorbed water is held as a condensed phase in the interstices or capillaries of the colloid and it is greatly dependent upon temperature and humidity.

- Occluded water is entrapped in microscopic pockets spaced irregularly throughout solid crystals. These cavities frequently occur naturally in minerals and rocks.

- Water also may be present as a solid solution in which the water molecules are distributed homogeneously throughout the solid. For example, natural glasses may contain several percent moisture in this form.

Heat Source. There are several choices when heating to dryness. The heat source is often determined by the amount of time available for drying and the potential for the sample to spatter or splash during drying. When time is not a primary concern and there is little or no chance of sample cross-contamination, samples are heated uncovered in a drying oven at the minimum temperature needed to remove moisture. If time is of concern, samples with high moisture content can usually be dried or evaporated faster using a hot plate. Heating on a hot plate significantly increases the chance of cross-contamination by spattering or splashing during boiling. However, ribbed watch glasses, which cover the sample yet still allow for evaporation, can be used to minimize cross contamination in this approach. Samples may also be placed under a heat lamp. This method reduces the risk of cross-contamination by applying heat to the surface where vaporization occurs, minimizing splashing during boiling. However, the elevated temperature is difficult to measure or control, and spattering still may be a problem when the sample reaches dryness.

Microwave systems may also be used to dry samples. ASTM E1358 and ASTM D4643 use microwave energy to dry either wood or soil to a constant weight. In a similar fashion, AOAC Methods 985.14 and 985.26 use microwave energy to dry fat from meat or water from tomato juice. Other examples include Beary (1988) who has compared microwave drying to conventional techniques using NIST solid standards (coal, clays, limestone, sediment) and foods and food materials (rice and wheat flour) standards and Koh (1980) who discusses microwave drying of biological materials.

Container Material. A sample container's material composition typically poses no problem. Borosilicate glass is generally recommended because it is inexpensive, transparent, reusable, and has good thermal properties. Platinum, Teflon™ (polytetrafluoroethylene—PTFE), porcelain, or aluminum foil containers are acceptable and may be preferable in certain situations. Polyethylene and other plastics of low melting point are only useful in hot water baths or ovens where the temperature is closely monitored. If polyethylene is going to be used, be aware that it is affected by heat applied directly to the container. The properties of several common materials used for sample containers are presented in Table 12.2 (on page 12-5). Note that the sample containers commonly received from the field will be those suitable for bulk samples rather than containers used during sample preparation. The plan will identify the type of container material to be used for field activities for samples to be shipped to the laboratory and the type of container material to be used during the various steps of sample preparation.

Heating Rate. The heating rate is generally not considered when removing moisture, because the maximum temperature typically is very low (60° to 110° C). Samples simply are placed inside the preset oven. Hot plates may be preheated to the desired temperature before heating the sample or turned on and gradually heated with the sample in place.

Maximum Temperature. The maximum temperature used for drying samples typically is just above the boiling point of water—105° to 110° C. Higher temperatures will not dry the samples significantly faster and may result in accidents or cross-contamination due to uneven heating. Lower temperatures will not reduce the chance of cross-contamination, but will significantly increase the drying time. One exception to this rule occurs when the physical form of the sample needs to be preserved. Many minerals and chemicals have waters of hydration that affect the structure and may also affect the chemical and physical properties. Samples heated at 60° C will retain the waters of hydration in most chemicals and minerals and still provide dry samples in a reasonable period of time (e.g., 12 to 15 hrs.).

Time. The duration a sample is heated to remove moisture depends on the size of the sample, the amount of moisture in the sample, the air flow around the sample, and the temperature applied to the sample. If heating the sample is to provide a constant dry weight, it is more difficult to determine how long to heat the sample. One convenient approach, especially when working with numerous samples, is to dry all materials overnight, or occasionally longer. This amount of heating is usually more than sufficient for drying samples for radiochemical analysis. If time is a critical factor or if a quantitative assessment of the uncertainty in the sample weight is required by the planning documents, the sample can be subjected to repeated cycles of drying and weighing until a series of weights meet the specified requirements (Section 12.3.1.3). For example, one such requirement might be to obtain three consecutive weights with a standard

deviation less than 5 percent of the mean. While repeated cycles of drying and weighing can provide a quantitative measure of the uncertainty in the sample weight over time, a single weight after an overnight drying cycle typically provides a similar qualitative level of confidence with significantly less working time. Another time-saving step is to use microwave techniques rather than conventional heating sources during sample preparation (ANL/ACL, 1992; Walter et al., 1997).

Alternatives to Heating. (1) Vacuum-desiccation. A desiccator is a glass or aluminum container that is filled with a substance that absorbs water, a "desiccant." The desiccator provides a dry atmosphere for objects and substances. Dried materials are stored in desiccators while cooling in order to minimize the uptake of ambient moisture. The ground-glass or metal rim of the desiccator should be greased lightly with petroleum jelly or silicone grease to improve performance. Calcium sulfate, sodium hydroxide, potassium hydroxide, and silica gel are a few of the common desiccants. The desiccant must be renewed frequently to keep it effective. Surface caking is a signal to renew or replace the desiccant. Some desiccants contain a dye that changes color upon exhaustion.

Vacuum desiccators are equipped with a side-arm so that they may be connected to a vacuum to aid in drying. The contents of the sealed evacuated desiccator are maintained in a dry, reduced-pressure atmosphere. Care must be exercised when applying a vacuum as a rapid pressure reduction, for high water content samples can result in "boiling" with subsequent sample loss and potential cross-contamination.

(2) Freeze-drying. Certain substances (i.e., biological materials, pharmaceuticals), which are extremely heat sensitive and cannot be dried at atmospheric conditions, can be freeze-dried (Cameron and Murgatroyd, 1996). Freeze-drying, also known as "lyophilization," is the process by which substances are frozen, then subjected to high vacuum. Under these conditions ice (water) sublimes and other volatile liquids are removed. The non-sublimable material is left behind in a dry state.

To freeze-dry effectively, dilute solutions are used. In order to increase the surface area, the material is spread out on the inner surface of the container as it is frozen. Once the solution or substance to be dried is frozen solid, the primary drying stage begins in which a high vacuum is applied, and the ice sublimes, desorbing the free ice and some of the bound moisture. During secondary drying, a prolonged drying stage, the sorbed water which was bound strongly to the solids, is converted to vapor. This can be a slow process because the remaining bound water has a lower pressure than the free liquid at the same temperature, making it more difficult to remove.

Secondary drying actually begins during the primary drying phase, but it must be extended after the total removal of free ice to achieve low levels of residual moisture.

Commercial freeze-drying units are self contained. Simple units consist of a vacuum pump, adequate vapor traps, and a receptacle for the material to be dried. More sophisticated models include refrigeration units to chill the solutions, instrumentation to designate temperature and pressure, heat and cold controls, as well as vacuum-release valves. The vacuum pump should be protected from water with a dry-ice trap and from corrosive gases with chemical gas-washing towers.

Charring of Samples to Partially Oxidize Organic Material

Heating samples at a moderate temperature (200° to 300° C) is sometimes used as a method of preparing a sample for subsequent decomposition using wet ashing or fusion techniques. Large amounts of organic material can react violently or even explosively during decomposition. Heating the sample to partially oxidize—or "char"—the organic material may limit reactivity during subsequent preparation.

Heat Source. Heat lamps, muffle furnaces, or hot plates may be used as a heat source for charring samples. Heat lamps are often selected because they can also be used to dry the sample before charring. Once dried, the sample can be moved closer to the lamp to raise the temperature and char the sample (confirmed by visual inspection). Heat lamps also reduce the potential for cross-contamination by minimizing spattering and splashing. Hot plates can be used similarly to heat lamps. The sample is dried and the temperature is raised to char the sample; however, hot plates increase the probability of spattering and splashing. Muffle furnaces can be used when the charring is performed as part of dry ashing instead of part of the drying process. In this case, the muffle furnace temperature is first raised slowly.

Sample Container. The choice of sample container depends primarily on the next step in the sample preparation process. When dry ashing or fusing, the sample container will usually be a platinum or porcelain crucible. Zirconium or nickel crucibles may also be used. If the sample will be dissolved using wet ashing techniques, the container may be borosilicate glass or a platinum crucible. Care should be taken to prevent ignition of samples in glass containers. Ignited samples may burn at temperatures high enough to cause damage to the container and loss of sample. Polyethylene and Teflon™ generally are not acceptable because of the increased temperature and risk of melting the container.

Heating Rate. Heating rate becomes a concern when charring samples because of the increased temperatures. The general rule is to raise the temperature slowly to heat the sample evenly and prevent large increases in temperature within the sample, which could lead to ignition. Typically, a rate of 50° to 100° C per hour is considered appropriate. Samples containing large quantities of organic material may require slower heating rates.

Maximum Temperature. One of the primary goals of charring a sample is to oxidize the materials slowly and gently. Gentle oxidation is accomplished by slowly raising the temperature close to the ignition point and letting the sample smolder. Many organic compounds ignite in the range of 200° to 300° C (e.g., paper burns at 230° C), so this is usually the range of temperatures where charring takes place. Ignition results in rapid oxidation accompanied by large volumes of released gases and potential sample loss. This reaction can raise the temperature of the sample to several hundred degrees above the desired maximum and result in significant losses during off-gassing. The progress of the reaction can be monitored visually by observing the volume of gas or smoke released. Thin wisps of smoke are usually allowable; clouds of smoke and flames are not. Visual inspection is easily accomplished when hot plates or heat lamps are used as heat sources. Some muffle furnaces are fitted with viewing windows to allow visual inspection. Never open a muffle furnace just to check on the progress of a reaction. This will cause a sudden change in temperature, increase the oxygen level and possibly ignite the sample, and disrupt air currents within the furnace to increase potential sample loss.

Time. The duration required to char a sample depends on the sample size, the amount of organic material in the sample, the ignition point of the organic material, the temperature of the sample, and the oxygen supply. Samples usually are heated until smoke begins to appear and allowed to remain at that temperature until no more smoke is evident. This process is repeated until the temperature is increased and no more smoke appears. Charring samples may require a significant amount of time and effort to complete. The duration may be reduced by improving the flow of air to the sample or mixing HNO_3 or nitrate salts with the sample before drying. However, this approach is recommended only for well-characterized samples, those previously evaluated for the applicability of this technique, because nitrated organic compounds can oxidize in a violent or explosive manner.

Dry Ashing Samples

The object of dry ashing is to combust all of the organic material and to prepare the sample for subsequent treatment using wet ashing or fusion techniques. This procedure involves heating a sample in an open dish or crucible in air, usually in a muffle furnace to control the temperature and flow of air. Microwave techniques are also available for dry ashing samples.

Dry ashing is used to determine ash weight as well as nonvolatile constituents. The associated chemistry is very complex, with oxidizing and reducing conditions varying throughout the sample and over time. During the combustion process, temperatures in the sample may reach several hundred degrees above the desired temperature, particularly if there is good air flow at the beginning of the ashing process (Bock, 1979). Covering samples during heating is not recommended, especially when using platinum crucibles. The lack of air produces a reducing atmosphere that results in reduction of metals that alloy with the crucible (Table 12.2 on page 12-5). This reaction results in loss of sample and potential for contamination of subsequent samples when using the same crucible.

Heat Source. The traditional heat sources for dry ashing are muffle furnaces or burner flames. Electronic muffle furnaces are recommended for all heating of platinum crucibles because burners produce significant levels of hydrogen gas during combustion, and platinum is permeable to hydrogen gas at elevated temperatures. Hydrogen gas acts as a reducing agent that can result in trace metals becoming alloyed to the platinum.

Microwave ovens have also proved to be quick and efficient when dry ashing plant tissue samples, with results comparable to conventional resistance muffle furnaces (Zhang and Dotson, 1998). The microwave units are fitted with ashing blocks (a ceramic insert) which absorb microwave energy and quickly heats to high temperatures. This, in combination with the microwave energy absorbed directly by the sample, allows for rapid dry ashing of most materials. The units are designed for increased air flow which further accelerates combustion of the samples.

Sample Container. Platinum, zirconium, or porcelain are usually used to form crucibles for dry ashing. Nickel may also be appropriate for some applications (Table 12.2). Platinum generally is recommended when available and is essentially inert and virtually unaffected by most acids. Zirconium and porcelain crucibles are resistant to most acids, are more resistant to HCl, and are significantly less expensive than platinum. Glass and plastic containers should not be used for dry ashing because the elevated temperatures exceed the melting point of these materials.

Crucibles fabricated from ceramic, graphite, and platinum can be used in microwave applications. Quartz fiber crucibles can accelerate the ashing process since this material rapidly cools and allows many sample types to be reweighed in 60 seconds or less after removal from the microwave unit.

Heating Rate. Samples should be dried before dry ashing and placed in an unheated furnace; then, the furnace temperature is gradually increased. The sample should be spread as thinly and

evenly as possible on the bottom of the container to allow for its equal heating. To ensure even heating of the sample and to minimize the chance of ignition, the temperature of the furnace is raised slowly. If the sample was previously charred, a rate of approximately 100° C per hour is typical. This rate is slow enough that small amounts of organic material or water can be removed from the sample without violent reactions. If the sample is not charred and contains a significant amount of organic material, a slower rate may be necessary to control the oxidation of organic material.

Maximum Temperature. The maximum temperature is determined by the sample matrix and the volatility of the elements to be analyzed. Generally, the temperature should be as low as possible to reduce the loss of volatile compounds, but high enough to ensure complete combustion of the sample. A minimum temperature of 450° C is often used to ensure complete combustion (Bock, 1979). The upper limit for dry ashing is usually determined by the sample container and the elements being analyzed and is generally considered to be 750° C, but sample-specific conditions may use temperatures up to 1,100° C. However, in practice, some components which are normally considered to be nonvolatile may be lost at temperatures above 650° C (Bock, 1979). Ashing aids may be added to samples to accelerate oxidation, prevent volatilization of specific elements, and prevent reaction between the sample and the container. Examples include adding nitrate before drying to assist oxidation and loosen the ash during combustion, adding sulfate to prevent volatilization of chlorides (e.g., $PbCl_2$, $CdCl_2$, NaCl) by converting them to the higher boiling sulfates, and adding alkaline earth hydroxides or carbonates to prevent losses of anions (e.g., Cl^-, As^{-3}, P^{-3}, B). Table 12.3 lists dry ashing procedures using a platinum container material for several elements commonly determined by radiochemical techniques.

TABLE 12.3 — Examples of Dry-Ashing Temperatures (Platinum Container)

Element	Temperature/Matrix
Cobalt	450° to 600° C for biological material; some losses reported owing to reactions with crucible; increased volume of sample increases volume of ash and limits loss of sample.
Cesium	400° to 450° C for food and biological material; CsCl and $CsNO_3$ volatilize at temperatures above 500° C.
Iodine	400° to 500° C with an alkaline ashing aid to prevent volatilization; losses reported as low as 450° C; total volatilization >600° C.
Lead	450° to 500° C acceptable for most samples; bone or coal (lead phosphate) may be ashed as high as 900° C without significant losses; PbO_2 reacts with silica in porcelain glaze at low temperatures; $PbCl_2$ is relatively volatile and nitrate or sulfate ashing aids have been used to good effect.
Plutonium	450° C with nitric acid ashing aid for biological material, 550° C for dust on air filters, 700° C for soil; high temperature leads to adsorption onto carbon particles and incomplete dissolution of ash.
Strontium	450° to 550° C for plants, 600° C for meat, 700° C for milk and bone.

- After a weight has been put on or taken off of the pan, the balance is allowed to settle for about 1 minute before a reading is taken.

- When possible, an electronic balance is used for recording the masses through a cable linked to a computer. In the absence of an electronic balance, two operators are used to read and record the masses.

- Moisture absorption models are assessed for realistic extrapolation to the time when the sample was taken from the desiccator, and uncertainties are assigned at $t = 0$ and for differences among models.

- All decimal places are carried until the final value is reported.

- Replicate drying of several samples are used to validate the efficacy of the drying protocol before routine use.

Among this list, major contributors to uncertainty are reaching stoichiometric consistency in the dried sample, calibration of the balance, fluctuation and drift in the balance operation, and curve-fitting moisture absorption corrections. These sources of measurement uncertainties should be quantified by measurement, inference, or judgement, then combined in quadrature as the mass uncertainty.

12.3.1.4 Subsampling

Laboratories routinely receive larger samples than required for analysis. The challenge then becomes to prepare a sample that is representative and large enough for analysis, but not so large as to cause needless work in its final preparation. Generally, a raw sample first is crushed to a reasonable particle size and a portion of the crushed material is taken for analysis. This step may be repeated with intermittent sieving of the material until an appropriate sample size is obtained. Then, this final portion is crushed to a size that minimizes sampling error and is fine enough for the dissolution method (Dean 1995; Pitard, 1993).

French geologist Pierre Gy (1992) has developed a theory of particulate sampling, which is applicable to subsampling in the laboratory. Appendix F summarizes important aspects of the theory and includes applications to radiochemistry. Some of the important points to remember include the following:

- For most practical purposes, a subsample is guaranteed to be unbiased only if every particle in the sample has the same probability of being selected for the subsample.

- The weight of the subsample should be many times greater than the weight of the largest particle in the sample.

- The variance associated with subsampling may be reduced either by increasing the size of the subsample or by reducing the particle sizes before subsampling.

- Grouping and segregation of particles tends to increase the subsampling variance.

- Grouping and segregation can be reduced by increment sampling, splitting, or mixing.

Increment sampling is a technique in which the subsample is formed from a number of smaller portions selected from the sample. A subsample formed from many small increments will generally be more representative than a subsample formed from only one increment. The more increments the better. An example of increment sampling is the one-dimensional "Japanese slab-cake" method (Appendix F).

Splitting is a technique in which the sample is divided into a large number of equal-sized portions and several portions are then recombined to form the subsample. Splitting may be performed by a manual procedure, such as fractional shoveling (Appendix F), or by a mechanical device, such as a riffle splitter. A riffle splitter consists of a series of chutes directed alternately to opposite sides. The alternating chutes divide the sample into many portions, which are then recombined into two. The riffle may be used repeatedly until the desired sample size is obtained. Riffle splitters are normally used with free-flowing materials such as screened soils.

Another traditional method for splitting is coning and quartering (Appendix F). Gy (1992) and Pitard (1993) do not recommend coning and quartering because with similar tools and effort, one can do fractional shoveling, which is a more reliable method.

If proper techniques and tools are used and adequate care is taken, samples of the sizes typically encountered in the laboratory can be mixed effectively. However, the effects of mixing tend to be short-lived because of the constant influence of gravity. Heterogeneous material may begin to segregate immediately after mixing.

The method and duration needed to mix a sample adequately depends on the volume and type of material to be mixed. Small volumes can be mixed by shaking for a relatively short time. Large

763 volumes may require hours. Pitard (1993) describes dynamic and discontinuous processes for
764 mixing samples including:

765 • Mechanical mixing of test tube samples is useful for small sample size and can be performed
766 on many samples at once. Some examples are a pipette shaker with a motor-activated,
767 rocking controlled motion; a nutator mixer with the test tubes fixed to an oscillating plate;
768 and a tube rotator where tubes are attached to a rotating plate mounted at an angle.

769 • Mechanical mixing of closed containers by rotating about a tumbling axis. A turbula
770 mechanical mixer is an example.

771 • Magnetic stirrers are commonly used to homogenize the contents of an open beaker.

772 • V-blenders are used to homogenize samples from several hundred grams to kilogram size.

773 • Stirrers coupled with propellers or paddles are used to mix large volumes of slurries or pulp.

774 • Sheet mixing or rolling technique, in which the sample is placed on a sheet of paper, cloth, or
775 other material, and the opposite corners are held while rolling the sample (see ASTM C702
776 for aggregates).

777 • Ball and rod mills homogenize as well as grind the sample (see ASTM C999 for soils).

778 When dealing with solid samples, it is often necessary to grind the sample to reduce the particle
779 size in order to ensure homogeneity and to facilitate attack by reagents. The *SPEX CertiPrep*
780 *Handbook of Sample Preparation and Handling* (Obenauf et al., website reference) is an
781 excellent resource for information regarding grinding and blending.

782 For hand grinding, boron carbide mortars and pestles are recommended. For samples which can
783 be pulverized by impact at room temperature, a shatterbox, a mixer-mill, or a Wig-L-Bug™ is
784 appropriate, depending on the sample size. For brittle materials—such as wool, paper, dried
785 plants, wood, and soft rocks—which require shearing as well as impact, a hammer-cutter mill is
786 warranted. For flexible or heat-sensitive samples such as polymers, cereal grains, and biological
787 materials, cryogenic grinding is necessary. Methods are described below:

788 • A shatterbox spins the sample, a puck, and a ring inside a dish-shaped grinding container in a
789 tight, high-speed horizontal circle. Within two to five minutes, approximately 100 grams of
790 brittle material can be reduced to less than 200 mesh. Shatterboxes are typically used to grind

soils, cement mix, rocks, slags, ceramics, and ores. They have also been used for hundreds of other materials including dried marsh-grass, pharmaceuticals, fertilizers, and pesticides. When used in a cryogenic atmosphere, this approach can be used to grind rubber, polymers, bone, hair, and tissue.

- A mixer-mill grinds samples by placing them in a container along with one or more grinding elements and imparting motion to the container. The containers are usually cylindrical, and the grinding elements are ordinarily balls, but may be rods, cylinders or other shapes. As the container is rolled, swung, vibrated or shaken, the inertia of the grinding elements causes them to move independently into each other and against the container wall, thus, grinding the sample. Mixer-mills are available for a wide-range of sample sizes. The length of time necessary to grind a sample depends on the hardness of the material and the fineness desired in the final product.

- The Wig-L-Bug™ is an effective laboratory mill for pulverizing and blending very small samples, typically in the range of 0.1 to 1 mL.

- A hammer-cutter mill utilizes high-speed revolving hammers and a serrated grinding chamber lining to combine both shearing and impact. A slide at the bottom of the hopper feeds small portions of the sample (up to 100 mL) into the grinding chamber. After the sample is adequately pulverized, it passes through a perforated-steel screen at the bottom of the grinding chamber and is then collected. With this approach, dried plants and roots, soils, coal and peat, chemicals, and soft rocks all grind quickly with little sample loss.

- Many analytical samples—such as polymers, rubber, and tissues that are too flexible or susceptible to degradation to be impact-ground at room temperature—can be embrittled by chilling, and then pulverized. Samples can be frozen and placed in a traditional grinder, or alternatively, a freezer mill can be utilized. In a freezer mill, the grinding vial is immersed in liquid nitrogen and an alternating magnetic field shuttles a steel impactor against the ends of the vial to pulverize the brittle material. Researchers at Los Alamos National Laboratory (LANL) developed a method of cryogenic grinding of samples to homogenize them and allow the acquisition of a representative aliquant of the materials (LANL, 1996).

When samples agglomerate or "cake" during grinding, further particle size reduction is suppressed. Caking can be caused from moisture, heat, static charge accumulation, the fusing of particles under pressure, etc. When it occurs, caking is a serious challenge. There are two main approaches to this problem, slurry grinding and dry grinding.

- In slurry grinding, particles are suspended in solution during grinding. Water, alcohol, or other liquids are added to the sample before grinding, and have to be removed afterwards. Slurry grinding is a fairly reliable way of grinding a sample to micron-sized particles, but it is sloppy and time-consuming.

- Dry grinding is often simpler and quicker, but requires careful matching of the technique to the sample. If caking is due to moisture, as in many soils or cements, the sample should be dried before grinding. Grinding aids such as lubricants, antistatic agents, abrasives, and binding agents can also be used. Examples of grinding aids include dry soap or detergent (a lubricant), graphite (an antistatic agent as well as a lubricant), polyvinyl alcohol, phenyl acetate, propylene glycol, and aspirin. For example, propylene glycol (one drop for up to ten grams of sample) is used for laboratory fine grinding of Portland cement and many minerals.

Grinding efficiency can be improved through intermittent screening of the material. The ground sample is placed upon a wire or cloth sieve that passes particles of the desired size. The residual particles are reground and this process is repeated until the entire sample passes through the screen. Sieves with large openings can be used in the initial stages of sample preparation to remove unwanted large rocks, sticks, etc.

12.3.2 Soil/Sediment Samples

For many studies, the majority of the solid samples will be soil/sediment samples or samples that contain some soil. The definition of soil is given in Chapter 10 (*Field and Sampling Issues that Affect Laboratory Measurements*). Size is used to distinguish between soils (consisting of sands, silts, and clays) and gravels.

The procedures to be followed to process a raw soil sample to obtain a representative subsample for analysis depend, to some extent, upon the size of the sample, the amount of processing already undertaken in the field, and more importantly, the radionuclide of interest and the nature of the contamination. Global fallout is relatively homogeneous in particle size and distribution in the sample, and therefore, standard preparation procedures should be adequate for this application. However, when sampling accidental or operational releases, the standard procedures may be inadequate. Transuranic elements, especially plutonium, are notorious for being present as "hot-spots" ions (Eberhardt and Gilbert, 1980; Sill, 1975) and great care must be employed so that the subsample taken for analysis accurately represents the total sample. This will depend on the size and the degree of homogeneity. Multiple subsampling, larger aliquants, and multiple analysis may be the only techniques available to adequately define the content of radionuclides in

heterogeneous samples. Therefore, it is imperative that the analyst choose a preparation approach appropriate to the nature of the sample.

12.3.2.1 Soils

ASTM has developed a Standard Practice for the preparation of soil samples (ASTM C999). Guidance is given in this ASTM method for the preparation of a homogenous soil sample from composited core samples. The soil samples are dried at 110° C until at constant weight, ground and mixed in a ball mill, and processed through a U.S. Series No. 35 (500-µm or 32-mesh) sieve. This method is intended to produce a homogeneous sample from which a relatively small aliquant (10 g) may be drawn for radiochemical analyses.

A similar procedure for homogenizing soil samples is given in HASL-300 (DOE, 1997). Unwanted material (e.g, vegetation, large rocks) is removed as warranted, and the sample is dried. If the sample contains small rocks or pebbles, the entire soil sample is crushed to 6.35 mm, or the entire sample is sieved through a 12.7-mm screen. The sample is blended, then reduced in size by quartering. This subsample of soil is processed through a grinder, ball mill, sieve, or pulverizer until the soil is reduced to <1.3 mm (15 mesh equivalent).

Sill et al. (1974) described a procedure where they dried raw soil samples for two to three hours at 120° C and then ground the cooled sample lightly in a mortar and pestle. All rocks larger than ¼ inch were removed. The sample was charred at 400° C for two to three hours, cooled and passed though a No. 35 U.S. standard sieve, and then blended prior to aliquanting (10.0 g are taken for the analysis).

12.3.2.2 Sediments

ASTM D3976 is a standard practice for the preparation of sediment samples for chemical analysis. This ASTM practice describes the preparation of test samples collected from streams, rivers, ponds, lakes, and oceans. The procedures are applicable to the determination of volatile, semivolatile, and nonvolatile constituents of sediments. Samples are first screened to remove foreign objects and then mixed by stirring. The solids are allowed to settle and the supernatant liquid is decanted. To minimize stratification effects due to differential rates of settling, the sample is mixed again before aliquanting for drying and analysis.

12.3.3 Biota Samples

12.3.3.1 Biological Samples

ASTM D4638 is a standard guide for the preparation of biological samples for inorganic chemical analysis. This ASTM guide gives procedures for the preparation of test samples of plankton, mollusks, fish, and plants. The preparation techniques are applicable for the determination of volatile, semivolatile, and nonvolatile inorganic compounds in biological materials. However, different preparation steps are involved for the three classes of inorganic compounds. In the case of nonvolatile compounds, the first step is to remove foreign objects and most of the occluded water. For large samples such as fish, samples are homogenized using a tissue disrupter, blender, or equivalent, and a moisture determination is performed on a one to two gram aliquant. The samples then are dried by heating in an oven, by dessication, by air drying, by freeze drying, or by low-temperature drying using an infrared lamp, hot plate, or a low setting on a muffle furnace. Finally, the samples are dry ashed.

12.3.3.2 Food

The International Atomic Energy Agency has provided a guidebook for the measurement of radionuclides in food and the environment (IAEA, 1989). Sample preparations for milk and other foods such as meat, fish, fruit, vegetables, and grains are given in this guidebook. Additionally, methods are presented in HASL-300 for the preparation of milk, vegetables, composite diets, etc. These methods generally involve dry ashing. The samples first are dried thoroughly at 125° C. Then, the temperature is raised at intervals over an 8-hour period through the critical range where ignition occurs, and finally to 500° C for 16 hours. If only a portion of ash is to be used for analysis, it is ground and sieved prior to aliquanting.

12.3.3.3 Vegetation

There are several DOE site references that contain examples of sample preparation for vegetation. Los Alamos National Laboratory (LANL, 1997) recently grew pinto beans, sweet corn, and zucchini squash in a field experiment at a site that contained observable levels of surface gross gamma radioactivity within Los Alamos Canyon. Washed edible and nonedible crop tissues (as well as the soil) were prepared for analysis for various radionuclides. Brookhaven National Laboratory has also evaluated the effect of its operation on the local environment. Their site environmental report (DOE, 1995) gives sample preparation steps for radionuclide analysis of vegetation and fauna (along with ambient air, soil, sewage effluent,

surface water, and groundwater). HASL-300 also describes sample preparation techniques for vegetation samples for a variety of radionuclides.

TABLE 12.4—Preliminary Ashing Temperature for Food Samples
(Method Sr-02-RC, HASL-300 [DOE, 1997])

Material	Temperature (° C)
Eggs	150-250
Meat	Burning
Fish	Burning
Fruit (fresh)	175-325
Fruit (canned)	175-325
Milk (dry)	—
Milk (wet)	175-325
Buttermilk (dry)	—
Vegetables (fresh)	175-225
Vegetables (canned)	175-250
Root vegetables	200-325
Grass	225-250
Flour	Burning
Dry beans	175-250
Fruit juices	175-225
Grains	225-325
Macaroni	225-325
Bread	225-325

12.3.3.4 Bone and Tissue

Bone and tissue samples can be dry ashed in a muffle furnace (HASL-300, Fisenne, 1994; Fisenne et al.,1980), wet ashed with nitric acid and peroxide (Fisenne and Perry, 1978) or alternately dry ashed and wet ashed with nitric acid until all visible signs of carbonaceous material has disappeared (McInroy et al., 1985).

12.3.4 Other Samples

The category "other" includes such matrices as concrete, asphalt, coal, plastic, etc. The sample preparation procedures applied to soils are generally applicable for the "other" category, except for more aggressive grinding and blending in the initial step. For example, items such as plastic or rubber which are too flexible to be impact-ground at room temperature must be ground cryogenically. They are embrittled by chilling and then pulverized. ASTM C114 describes the sample preparation steps for the chemical analysis of hydraulic cement, whereas ASTM C702 describes the sample preparation of aggregate samples, and is also applicable to lime and limestone products as noted in ASTM C50. Additionally, ASTM D2013 describes the preparation of coal samples for analysis.

12.4 Filters

Filters are used to collect analytes of interest from large volumes of liquids or gases. The exact form of the filter depends on the media (e.g., air, aqueous liquid, nonaqueous liquid), the analyte matrix (e.g., sediment, suspended particulates, radon gas), and the objectives of the project (e.g., volume of sample passing through the filter, flow rate through the filter, detection limits, etc. (see the section on filtration in Chapter 10, *Field and Sampling Issues that Affect Laboratory Measurements*).

946 Filter samples from liquids usually consist of the filter with the associated solid material. For
947 samples with a large amount of sediment, the solid material may be removed from the filter and
948 analyzed as a solid. When there is a relatively small amount of solid material, the filter may be
949 considered as part of the sample for analytical purposes. When large volumes of liquid are
950 processed at high flow rates, filter cartridges often are used. Typically, the cartridge case is not
951 considered part of the sample, and laboratory sample preparation includes removing the filter
952 material and sample from the cartridge case. Any special handling instructions should be
953 included as SOPs in the planning documents.

954 Air filters may be particulate filters, which are prepared in the same manner as liquid filters, or
955 they may be cartridges of absorbent material. Filters that absorb materials are typically designed
956 for a specific analysis. For example, activated charcoal cartridges are often used to collect
957 samples of iodine or radon. Silver zeolite cartridges may be used for noble gases such as argon,
958 krypton, or xenon. These cartridges are often designed to be analyzed intact, so no special sample
959 preparation is needed. If the cartridges need to be disassembled for analysis, a special SOP for
960 preparing these samples is usually required.

961 Homogenization is rarely an issue when preparing filter samples. Typically, the entire filter is
962 digested and analyzed. However, obtaining a representative sample of a filter does become an
963 issue when the entire filter is not analyzed. The planning document should give the details of
964 sample preparation for portions of a filter (e.g., sample size reduction through quartering). Steps
965 such as using tweezers for holding filters and using individual sample bags should be taken to
966 prevent the loss of material collected on the filter during handling and processing.

967 12.5 Wipe Samples

968 Wipe samples (also referred to as "swipes" or "smears") are collected to indicate the presence of
969 removable surface contamination. The loose contamination is transferred from the surface to a
970 sample of wipe material. The wipe material can be virtually anything, but common materials
971 include Whatman filter paper and nylon membrane. The greatest challenge in preparing wipe
972 samples is homogenizing the sample to obtain a representative portion for analysis, although
973 usually the entire wipe is analyzed. Wipe samples are commonly digested prior to analysis, but
974 they can be analyzed directly through appropriate counting techniques (McFarland, 1998a,
975 1998b).

976 Many wipe samples are collected using filter paper or disc smears. In many cases, the
977 contamination on these samples is simply assumed to be fairly evenly distributed, and the wipe
978 samples are prepared like filter samples. Sometimes, a specific analytical procedure is anticipated

and a special wipe material is used. For example, Styrofoam generates static electricity and can attract dust particles from a relatively clean surface. Styrofoam is dissolved easily in most (if not all) commercially available liquid scintillation cocktails. These wipe samples can be very easily collected, stored, and transported in liquid scintillation vials. Have the cocktail added by the laboratory and be counted for gross alpha and gross beta activity using a liquid scintillation counter.

12.6 Liquid Samples

Liquid samples are commonly classified as aqueous, nonaqueous, and mixtures. Aqueous liquids are most often surface water, groundwater, drinking water, precipitation, effluent, or runoff. Nonaqueous liquids may include solvents, oils, or other organic liquids. Mixtures may be combinations of aqueous and nonaqueous liquids, but may include solid material mixed with aqueous or nonaqueous liquids or both.

Preliminary sample measurements (e.g., conductivity, turbidity) may be performed to provide information about the sample and to confirm field processing (see measurement of pH to confirm field preservation in Chapter 11). These measurements are especially useful when there is no prior historical information available from the sample collection site. In addition, this information can also be helpful in the performance of certain radiochemical analyses. These preliminary measurements typically require little or no sample preparation. In many cases, the results of preliminary measurements can be used to determine the quantity of sample to be used for a specific analysis.

12.6.1 Conductivity

In radiochemistry, conductivity measurements typically are used as a surrogate to estimate dissolved solids content for gross-alpha and gross-beta measurements. Because the preservation of samples with acid prevents the measurement of conductivity, the recommendation is to perform the QC checks for conductivity in the field when the original measurements are performed. If the sample is not preserved in the field, the measurement can be done in the laboratory.

ASTM D1125 is the standard test method for determining the electrical conductivity of water. The method is used for the measurement of ionic constituents, including dissolved electrolytes in natural and treated water.

12.6.2 Turbidity

The presence of dissolved or suspended solids, liquids, or gases causes turbidity in water. Measurement of turbidity provides a means to determine if removal of suspended matter is necessary in order to meet the specifications for liquid samples as given in the plan document. ASTM D1889 is the standard test method for the determination of turbidity of water and wastewater in the range from 0.05 to 40 nephelometric turbidity units (NTU). In the ASTM method, a photoelectric nephelometer is used to measure the amount of light that a sample scatters when the light is transmitted through the sample.

12.6.3 Filtration

The filtration of samples is based on the appropriate plan document which should also give the selection of the filter material to be used. If samples have not been filtered in the field, the laboratory can perform the filtration. Guidance on filtration of liquid samples is provided in Section 10.3.3. Filtering is normally done in the field so that preservatives can be added without promoting the dissolution of undissolved solids in the sample at the time of collection.

12.6.4 Aqueous Liquids

Aqueous liquids are a common matrix analyzed by laboratories, and are often referred to as *water samples*. Examples of possible aqueous liquids requiring radionuclide analysis include the following:

- Drinking water;
- Surface water;
- Ground water;
- Soil pore water;
- Storage tank water;
- Oil production water or brine;
- Trench or landfill leachate; and
- Water from vegetation.

For certain samples that are not filtered, inversion is a form of homogenization. Typically, the sample is homogenized by inverting the container several times to mix the sample thoroughly. If there is some air in the container, the passage of air bubbles through the sample will create sufficient turbulence to mix the sample thoroughly with three or four inversions of the sample container. If the sample contains zero headspace (so there is no air in the sample container), the

sample should be inverted and allowed to stay inverted for several seconds before the next inversion. Ten to twenty inversions of the sample container may be required to ensure that the sample is mixed thoroughly under zero headspace conditions. Simply shaking the container will not mix the contents as thoroughly as inverting the sample container. Mechanical shakers, mixers, or rotators may be used to homogenize aqueous samples thoroughly.

Filtration and acidification performed in the field is typically the only preparation required for aqueous liquids (Chapter 10). A general discussion concerning preparation of water samples for the measurement of radioactivity is presented in NCRP (1976). *Analytical Chemistry Laboratory Sample Preparation Methods* (ACL, 1992) gives a number of sample preparation methods for various materials, including water samples.

ASTM gives standard test methods for the preparation of water samples for the determination of alpha and beta radioactivity (ASTM D1943 and D1890, respectively). After collecting the water sample in accordance with ASTM D3370, the sample is made *radioactively homogeneous* by addition of a reagent in which the radionuclides present in the sample are soluble in large concentrations. Acids, complexing agents, or chemically similar stable carriers may be used to obtain homogeneity. The chemical nature of the radionuclides and compounds present and the subsequent steps in the method will indicate the action to be taken. Different preparation techniques for freshwater and seawater samples are illustrated in *Radiochemical Analytical Procedures for Analysis of Environmental Samples* (EPA, 1979) and for drinking water in EPA (1980).

12.6.5 Nonaqueous Liquids

Nonaqueous liquids can be substances other than water such as organic solvents, oil, or grease. Many organic solvents are widely used to clean oil, grease, and residual material from electrical and mechanical equipment. The resulting waste liquid may contain a significant amount of solid material. It may be necessary to filter such liquids to determine (1) if the analyte is contained in the filtrate and is soluble, or (2) if the analyte is contained in the solids and therefore is insoluble. The appropriate plan document should be reviewed to determine if filtration is necessary. ASTM C1234, Standard Test Method for *Preparation of Oils and Oily Waste Samples by High-Pressure, High-Temperature Digestion for Trace Element Determinations*, describes the preparation of homogeneous samples from nuclear processing facilities.

Homogenization of nonaqueous samples is accomplished in a manner similar to that for aqueous samples. Visual inspection is typically used as a qualitative measure of homogeneity in nonaqueous samples. If a quantitative measure of mixing is desired, turbidity measurements can

be performed after a predetermined amount of mixing (e.g., every 10 inversions, every 2 minutes, etc.) until a steady level of turbidity is achieved (e.g., 1 to 10 percent variance, depending on the project objectives—see ASTM D1889, *Standard Test Method for Turbidity of Water*).

DOE (ANL/ACL, 1995) evaluated sample preparation techniques used for the analysis of oils. In evaluating the performance of a sample preparation technique, DOE considered the following qualities to be important:

- Thorough sample decomposition;
- Retention of volatile analytes;
- Acceptable analyte recovery;
- Minimal contamination from the environment or the digestion vessel;
- Low reagent blanks; and
- Speed.

One of the preparation methods involved combustion of oil under oxygen at 25 atm pressure (ASTM E926) and another used nitric acid decomposition of the oil in a sealed vessel heated with a microwave (EPA, 1990).

Many nonaqueous liquids present a health hazard (e.g., carcinogenicity) or require special safety considerations (e.g., flammability). Any special handling requirements based on health and safety considerations should be documented in the planning documents.

12.6.6 Mixtures

Some common examples of mixtures that may be encountered by the laboratory are water with lots of total dissolved solids and undissolved solids or water and oil in separate layers. The following sections discuss preparation procedures for these types of mixtures.

12.6.6.1 Liquid-Liquid Mixtures

When aqueous and nonaqueous liquids are combined, they usually form an immiscible mixture, such as oil and water.[1] In most cases, a separatory funnel helps in separating the liquids into two

[1] It is often necessary to determine which liquid is aqueous and which liquid is nonaqueous. Never assume that the top layer is always nonaqueous, or the bottom layer is always aqueous. The density of the bottom layer is always greater than the density of the top layer. Halogenated solvents (e.g., carbon tetrachloride, CCl_4) tend to have

(continued...)

samples. Each sample then is analyzed separately. If, in the rare case, both liquids must be processed together, there is greater difficulty in preparing the combined liquids for analysis. Obtaining a homogenous aliquant is a key consideration in this case. Often times, the entire sample should be analyzed. This approach avoids processing problems and yields the desired result.

12.6.6.2 Liquid-Solid Mixtures

Mixtures of liquids and solids are usually separated by filtering, centrifuging, or decanting, and the two phases are analyzed separately. If the mixture is an aqueous liquid and a solid, and will be analyzed as a single sample, the sample is often treated as a solid. Completely drying the sample followed by dry ashing before any attempt at wet ashing is recommended to reduce the chance of organic solids reacting with strong oxidizing acids (e.g., H_2SO_4, HNO_3, etc.). If the mixture includes a nonaqueous liquid and a solid, it is suggested that the phases be separated by filtration and the solid rinsed thoroughly with a volatile solvent such as ethanol or methanol before continuing with the sample preparation process.

In rare cases where a sample contains a mixture of aqueous liquid, nonaqueous liquid, and solid material, the sample can be separated into three different phases before analysis. The sample should be allowed to settle overnight and the liquids decanted. The liquids can then be separated in a separatory funnel without the solid material clogging the funnel. Each liquid should be filtered to remove any remaining solid material. The solid should be filtered to remove any remaining liquid and rinsed with a volatile solvent. This rinse removes any traces of organic liquids to reduce problems during subsequent dissolution activities. The three phases are then analyzed separately. If necessary, the results can be added together to obtain a single result for the mixture after the separate analyses are completed.

12.7 Gases

Sample preparation steps are usually not required for gas samples. Lodge (1988) gives general techniques, including any necessary sample preparation, for the sampling and storage of gases

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[1](...continued)
densities greater than about 1 g/mL, so they typically represent the bottom layer. Other organic liquids (e.g., diethyl ether, oil, etc.) tend to have densities less than 1 g/mL, so they typically represent the top layer. Mixtures of organic liquids may have almost any density. To test the liquids, add a drop of water to the top layer. If the drop dissolves in the top layer, the top layer is aqueous. If the drop settles through the top layer and dissolves in the bottom layer, the bottom layer is aqueous.

and vapors. The determination of the tritium content of water vapor in the atmosphere is one of the example procedures. ASTM D3442 is a standard test method for the measurement of total tritium activity in the atmosphere. Sample preparation is covered in this test method.

EPA has prepared "Background Information Document: Procedures Approved for Demonstrating Compliance with 40 CFR Part 61" (EPA, 1989) for use in demonstrating compliance with the radionuclide National Emission Standards for Hazardous Air Pollutants (NESHAP). This document includes references to air sampling and sample preparation. Table 3-1 of EPA (1989) lists numerous references to radionuclide air sampling and preparation; examples include:

- *A Study of Airborne Radioactive Effluents from the Pharmaceutical Industry* (Cehn, 1979).
- "The Fraction of Material Released as Airborne Activity During Typical Radioiodinations," (Eichling, 1983).
- "Application for Renewal of Source Material License: SUB-526, Docket 40-3392," (Allied Chemical, 1982).
- "Airborne Concentrations of I-131 in a Nuclear Medicine Laboratory" (Browning et al., 1978).

12.8 Bioassay

Analyses of bioassay samples are necessary to monitor the health of employees involved in radiological assessment work. Normally these types of samples include urine and fecal specimens.

Urine samples are typically wet ashed with nitric acid (DOE, 1997; HASL-300) or with nitric acid and peroxide (RESL, 1982). Alternatively, there are procedures which co-precipitate the target analytes in urine by phosphate precipitation (Horwitz et al., 1990; Stradling and Popplewell, 1974; Elias, 1997). Fecal samples are normally dry ashed in a muffle furnace (HASL-300), or prepared by lyophilization, "freeze drying" (Dugan and McKibbin, 1993).

It is important to note that although ANSI 13.30 indicates that aliquanting a homogeneous sample to determine the activity present in the total sample is acceptable, this standard dictates that the entire sample should be prepared for analysis and the aliquant taken after the sample preparation has been completed.

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American Society for Testing and Materials (ASTM) C1234. Standard Test Method for *Preparation of Oils and Oily Waste Samples by High-Pressure, High-Temperature Digestion for Trace Element Determinations.*

American Society for Testing and Materials (ASTM) D1125. Standard Test Method for *Determining the Electrical Conductivity of Water.*

American Society for Testing and Materials (ASTM) D1889. Standard Test Method for *Turbidity of Water.*

American Society for Testing and Materials (ASTM) D1890. Standard Test Method for *Beta Particle Radioactivity of Water.*

American Society for Testing and Materials (ASTM) D1943. Standard Test Method for *Alpha Particle Radioactivity of Water.*

American Society for Testing and Materials (ASTM) D2013. Standard Method of *Preparing Coal Samples for Analysis.*

American Society for Testing and Materials (ASTM) D3370. Standard Practices for *Sampling Water from Closed Conduits.*

American Society for Testing and Materials (ASTM) D3442. Standard Test Method for *Gaseous Tritium Content of the Atmosphere.*

American Society for Testing and Materials (ASTM) D3974. Standard Practice for *Extraction of Trace Elements from Sediments.*

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13 SAMPLE DISSOLUTION

13.1 Introduction

The overall success of any analytical procedure depends upon many factors, including proper sample preparation, appropriate sample dissolution, and adequate separation and isolation of the target analytes. This chapter describes sample dissolution techniques and strategies. Some of the principles of dissolution are common to those of radiochemical separation that are described in the next chapter, but their importance to dissolution is reviewed in this chapter.

Sample dissolution can be one of the biggest challenges facing the analytical chemist, because most samples consist mainly of unknown compounds with unknown chemistries. There are many factors for the analyst to consider: What are the data quality objective requirements for bias and precision to meet the data quality objectives of the program? What is the nature of the sample; is it refractory or is there only surface contamination? How effective is the dissolution technique? Will any analyte be lost? Will the vessel be attacked? Will any of the reagents interfere in the subsequent analysis or can any excess reagent be removed? What are the safety issues involved? What are the labor and material costs? How much and what type of wastes are generated? The challenge for the analyst is to balance these factors and to choose the method that is most applicable to the material to be analyzed.

The objective of sample dissolution is to mix a solid or nonaqueous liquid sample quantitatively with water to produce an aqueous solution (homogeneous mixture),so that subsequent separation and analyses may be performed. Because very few natural or organic materials are water-soluble, these materials routinely require the use of acids or fusion salts to bring them into solution. These reagents typically achieve dissolution through an oxidation-reduction process that leaves the constituent elements in a more soluble form. Moreover, because radiochemists routinely add carriers or use the technique of isotope dilution to determine certain radioisotopes, dissolution helps to ensure exchange between the carrier or isotopic tracer and the element or radioisotope to be determined, although additional chemical treatment might be required to ensure exchange.

There are three main techniques for sample decomposition discussed in this chapter:

- Fusion;
- Wet ashing, acid leaching, or acid dissolution; and
- Microwave digestion.

Fusion and wet ashing techniques are used singly or in combination to decompose most samples analyzed in radioanalytical laboratories. Generally, fusion techniques are used when a total

dissolution of a difficult sample matrix is required. Leaching techniques are used to determine the soluble fraction of the radionuclide of interest under specific conditions. Because recent advances in microwave vessel design have allowed for the use of larger samples, microwave dissolution is becoming an important tool in the radiochemistry laboratory.

Because of the potential for injury and explosions, it is essential that proper laboratory safety procedures be in place, the appropriate safety equipment be available, a safe work space be provided, and that the laboratory personnel undergo the necessary training to ensure a safe working environment before any of these methods are used.

Aspects of proper sample preparation, such as moisture removal, oxidation of organic matter, and homogenization, were discussed in Chapter 12, *Laboratory Sample Preparation*. Fundamental separation principles and techniques, such as complexation, solvent extraction, ion exchange, and co-precipitation, are reviewed in Chapter 14, *Separation Techniques*.

There are many excellent references on the topic of sample dissolution, including *A Handbook of Decomposition Methods in Analytical* Chemistry (Bock, 1979), *Analytical Chemistry Handbook* (Dean, 1995), *Methods for Decomposition in Inorganic Analysis* (Sulcek and Povondra, 1989), and "A Decomposition and Dissolution of Samples: Inorganic" (Bogen, 1978).

13.2 The Chemistry of Dissolution

In order to dissolve a sample completely, each insoluble component must be converted into a soluble form. Several basic chemical methods are employed to accomplish complete dissolution of the sample, but usually the tracer is added to the sample. An outline of the principles of these chemical methods is provided in this section, but a complete description is available in Chapter 14 (*Chemical Separations*), where the principles are applied to a broader range of topics.

13.2.1 Solubility and the Solubility Product Constant, K_{sp}

The solubility data of many compounds, minerals, ores, and elements are available in reference manuals. Solubilities typically are expressed in grams of substance per 100 mL of solvent, although other units are used sometimes. The information is more complete for some substances than others, and for many substances solubility is expressed only in general terms, such as "soluble," "slightly soluble," or "insoluble." Many environmental samples consist of complex mixtures of elements, compounds, minerals, or ores, most of which are insoluble and must be treated chemically to dissolve completely. In some cases, the sample constituents are known to the analyst, but often they are not. Solubility data might not be available even for known

constituents, or the available data might be inadequate. Under these circumstances, sample dissolution is not a simple case of following the solubilities of known substances. For known constituents with solubility data, the solubilities indicate those that must be treated to complete dissolution. This, in turn, provides a guide to the method of treatment of the sample. Given the potential complexity of environmental samples, it is difficult to describe conditions for dissolving all samples. Sometimes one method is used to dissolve one part of the sample while another is used to dissolve the residue.

The solubility of many compounds in water is very low, on the order of small fractions of a grams per 100 mL. Instead, the solubility is often expressed by a solubility product constant (K_{sp}), an equilibrium constant for dissolution of the compound in water (see Section 14.8.3.1, "Solubility and Solubility Product Constant"). The solubility product constant for strontium carbonate, a highly insoluble salt (0.0006 g/100 mL), is the equilibrium constant for the process:

$$SrCO_3(s) \rightarrow Sr^{+2}(aq) + CO_3^{-2}(aq)$$

and is represented by:

$$K_{sp} = [Sr^{+2}][CO_3^{-2}] = 1.6 \times 10^{-9}$$

The brackets indicate the molar concentration (moles/liter) of the respective ions dissolved in water. The very small value of the constant results from the low concentration of dissolved ions, and the compound is referred to as "insoluble." Chemical treatment is necessary sometimes to dissolve the components of a compound in water. In this example, strontium carbonate requires the addition of an acid to solubilize Sr^{+2}. The next section describes chemical treatment to dissolve compounds.

13.2.2 Chemical Exchange, Decomposition, and Simple Rearrangement Reactions

Chemical exchange, decomposition, and simple rearrangement reactions refer to one method for solubilizing components of a sample. In this chemical process, the sample is treated to convert insoluble components to a soluble chemical species using chemical exchange (double displacement), decomposition, or simple rearrangement reactions rather than oxidation-reduction processes or complex formations. Some fluxes solubilize sample components using chemical exchange. Radium or strontium cations in radium or strontium carbonate ($RaCO_3$ or $SrCO_3$) exchange the carbonate anion for the chloride ion on acid treatment with HCl to produce the soluble chlorides; the carbonic acid product decomposes to carbon dioxide and water:

$$RaCO_3 + 2\ HCl \rightarrow RaCl_2 + H_2CO_3$$

$$H_2CO_3 \rightarrow CO_2 + H_2O$$

and the net reaction is as follows:

$$RaCO_3 + 2\ HCl \rightarrow RaCl_2 + CO_2 + H_2O$$

Sodium pyrosulfate fusion, for example, converts zirconia (ZrO_2) into zirconium sulfate [$Zr(SO_4)_2$], which is soluble in acid solution by a simple (nonoxidative) rearrangement of oxygen atoms (Hahn, 1961, p. 81; Steinberg, 1960, p. 4):

$$ZrO_2 + 2\ Na_2S_2O_7 \rightarrow 2\ Na_2SO_4 + Zr(SO_4)_2$$

Many environmental samples contain insoluble silicates, such as aluminum silicate [$Al_2(SiO_3)_3$ or $Al_2O_3 \cdot 3SiO_2$], which can be converted into soluble silicates by fusion with sodium carbonate:

$$Al_2(SiO_3)_3 + 4\ Na_2CO_3 \rightarrow 3\ Na_2SiO_3 + 2\ NaAlO_2 + 4\ CO_2$$

Dissolution of radium from some ores depends on the exchange of anions associated with the radium cation (sulfate for example) to generate a soluble compound. Extraction with nitric acid is partly based on this process, generating soluble radium nitrate.

13.2.3 Oxidation-Reduction Processes

Oxidation-reduction (redox) processes play an important role in sample dissolution because solubility is highly dependent not only on the chemical form of the element, but also on oxidation state. Moreover, many radiochemical procedures require the addition of a carrier and isotope tracer, and to achieve quantitative yields, there must be complete equilibration (isotopic exchange) between the added isotopes and all chemical species present. Dissolution of the sample in the presence of the appropriate carrier and/or tracer is one way to promote equilibration by exposing all components of the analytical mixture to the same redox conditions.

An oxidation-reduction reaction is a reaction that redistributes electrons among the atoms, molecules, or ions in the reaction. In some redox reactions, electrons actually are transferred from one reacting species to another. In other redox reactions, electrons are not transferred completely from one reacting species to another; the electron density about one atom decreases, while it increases about another atom. A complete discussion of oxidation and reduction is found in Section 14.2, "Oxidation/Reduction Processes."

Many oxidizing agents used in sample dissolution convert metals to a stable oxidation state displacing hydrogen from hydrochloric, nitric, sulfuric, and perchloric acids. (This redox process

often is referred to in the literature as nonoxidative hydrogen replacement by an active metal, but it is a redox process where the metal is oxidized to a cation, usually in its highest oxidation state, and the hydrogen ion is reduced to it elemental form.) Dissolution of uranium for analysis is an example of hydrogen-ion displacement to produce a soluble substance (Grindler, 1962, p. 252):

$$U + 8\,HNO_3 \rightarrow UO_2(NO_3)_2 + 6\,NO_2 + 4\,H_2O$$

Prediction of the reactivity of a metal with acids is dependent on its position in the electromotive force series (activity series). A discussion of the series appears in Section 13.4.1, "Acids and Oxidants." In general, metals below hydrogen in the reduction series will displace hydrogen from acid solution and be dissolved, while acids above the series will not. Perchloric acid offers a particular advantage because very soluble perchlorate salts are formed.

Other important oxidizing processes depend on either oxidizing a lower, less soluble oxidation state of a metal to a higher, more soluble state or oxidizing the counter anion to generate a more soluble compound. Oxidation to a higher oxidation state is common when dissolving uranium samples in acids or during treatment with fluxes. The uranyl ion (UO_2^{+2}) forms soluble salts—such as chloride, nitrate, and perchlorate—with anions of the common acids (Grindler, 1962, p. 255 and pp. 9-14). (Complex-ion formation also plays a role in these dissolutions; see the next section). Dissolution of oxides, sulfides, or halides of technetium by alkaline hydrogen peroxide converts all oxidation states to the soluble technate salts (Cobble, 1964,p. 418):

$$2\,TcO_2 + 2\,NaOH + 3\,H_2O_2 \rightarrow 2\,NaTcO_4 + 4\,H_2O$$

13.2.4 Complexation

The formation of complex ions (see also Section 14.3, "Complexation") is important in some dissolution processes and usually occurs in conjunction with treatment by an acid, but can also occur during fusion. Complexation increases solubility in the dissolution mixture and helps to minimize hydrolysis of the cation. The solubility of radium sulfate in concentrated sulfuric acid is the result of forming a complex-ion, $Ra(SO_4)_2^{-2}$. The ability of both hydrochloric and hydrofluoric acids to act as a solubilizing agent is dependent on their abilities to form stable complex ions with cations. Refractory plutonium samples are solubilized in a nitric acid-hydrofluoric acid solution forming cationic fluorocomplexes such as PuF^{+3} (Booman and Rein, 1962, p. 244). Numerous stable complexes of anions from solubilizing acids (HCl, HF, HNO_3, H_2SO_4, $HClO_4$) contribute to the dissolution of other radionuclides, such as americium, cobalt, technetium, thorium, uranium, and zirconium (see Section 14.10, "Radiochemical Equilibrium").

The process of fusion with sodium carbonate to solubilize uranium samples is also based on the formation of $UO_2(CO_3)_2^{-4}$ after the metal is oxidized to U^{+6} (Grindler, 1962, p. 256).

13.2.5 Equilibrium: Carriers and Tracers

Carriers and tracers that are required for radiochemical separation and detection procedures usually are added to samples before dissolution in order to subject them to the same chemical treatment as the analyte. Addition as soon as practical promotes equilibration with the analyte. The dissolution process tends to bring the carrier and tracers to the same oxidation state as the analyte and ensures intimate mixing of all the components in solution. Acid mixtures also create a large hydrogen-ion concentration that minimizes the tendency of cations to hydrolyze and subsequently form insoluble complexes. Detailed discussions of carriers and tracers as well as radiochemical equilibration are found in Section 14.9, "Carriers and Tracers" and Section 14.10, "Radiochemical Equilibration." Knowledge of the behavior of carriers and tracers and of the principles behind radiochemical equilibrium is very important, because the final form of the analyte in solution is crucial to understanding their behavior, not only during solubilization of the sample but also in the separation and detection steps of the analysis. During each of the steps in the method, the analyst should be aware of the expected oxidation states of the analyte and its tendency to hydrolyze, polymerize, and form complexes and radiocolloids, and other issues during each step of the procedure. Knowledge of these processes will ensure that the analyst will be able to recognize and address problems if they arise.

13.3 Fusion Techniques

Sample decomposition through fusion is most employed often for samples that are difficult to dissolve in acids such as soils, sludges, silicates, and some mineral oxides. Fusion is accomplished by heating a salt (the flux) mixed with a small amount of sample. The mixture is heated to a temperature above the melting point of the salt, and the sample is allowed to react in the molten mixture. When the reaction is completed, the mixture is allowed to cool to room temperature. The fused sample is then dissolved, and the analysis is continued. Any residue remaining may be treated by repeating the fusion with the same salt, performing a fusion with a different salt, wet ashing, or any combination of the three.

Decomposition of the sample matrix depends on the high temperatures required to melt a flux salt and the ratio of the flux salt to the sample. For a fusion to be successful, the sample must contain chemically bound oxygen as in oxides, carbonates, and silicates. Samples that contain no chemically bound oxygen, such as sulfides, metals, and organics, must be oxidized before the fusion process.

Samples to be fused should be oven-dried to remove moisture. Charring to remove organic material is not usually necessary because samples with significant amounts of organic material are typically dry ashed or wet ashed before fusion. Solid samples are ground mesh size to increase the surface area, allowing the fusion process to proceed more readily. The sample must be thoroughly mixed with the flux in an appropriate ratio. Generally, the crucible should never be more than half-filled at the outset of the fusion process. Fusions may be performed using sand or oil baths on a hot plate, in a muffle furnace, or over a burner. Crucibles are made of platinum, zirconium, nickel, or porcelain (Table 13.1). The choice of heat source and crucible material generally depends on the salt used for the fusion.

TABLE 13.1 — Common fusion fluxes

Flux (mp, °C)	Fusion Temperature, °C	Type of Crucible	Types of Sample Decomposed
$Na_2S_2O_7$ (403) or $K_2S_2O_7$ (419)	Up to red heat	Pt, quartz, porcelain	For insoluble oxides and oxide-containing samples, particularly those of Al, Be, Ta, Ti, Zr, Pu, and the rare earths.
NaOH (321) or KOH (404)	450-600	Ni, Ag, glassy carbon	For silicates, oxides, phosphates, and fluorides.
Na_2CO_3 (853) or K_2CO_3 (903)	900-1,000	Ni Pt for short periods (use lid)	For silicates and silica-containing samples (clays, minerals, rocks, glasses), refractory oxides, quartz, and insoluble phosphates and sulfates.
Na_2O_2	600	Ni; Ag, Au, Zr; Pt (<500 °C)	For sulfides; acid-insoluble alloys of Fe, Ni, Cr, Mo, W, and Li; Pt alloys; Cr, Sn, and Zn minerals.
H_3BO_3 (169)		Pt	For analysis of sand, aluminum silicates, titanite, natural aluminum oxide (corundum), and enamels.
$Na_2B_4O_7$ (878)	1,000-1,200	Pt	For Al_2O_3; ZrO_2 and zirconium ores, minerals of the rare earths, Ti, Nb, and Ta, aluminum-containing materials; iron ores and slags.
$Li_2B_4O_7$ (920) or $LiBO_2$ (845)	1,000-1,100	Pt, graphite	For almost anything except metals and sulfides. The tetraborate salt is especially good for basic oxides and some resistant silicates. The metaborate is better suited for dissolving acidic oxides such as silica and TiO_2 and nearly all minerals.
NH_4HF_2 (125) NaF (992) KF (857) or KHF, (239)	900	Pt	For the removal of silicon, the destruction of silicates and rare earth minerals, and the analysis of oxides of Nb, Ta, Ti, and Zr.

Source: Dean (1995) and Bock (1979).

Fusions are heated slowly and evenly to prevent ignition of the sample before the reaction with the molten salt can begin. It is especially important to raise the temperature slowly when using a

gas flame because the evolution of water and gases is a common occurrence at the beginning of the fusion, and hence a source of spattering. The crucible can be covered with a lid as an added precaution. Sand and oil baths provide the most even source of heat, but they are difficult to maintain at very high temperatures. Muffle furnaces provide an even source of heat, but when using them it is difficult to monitor the progress of the reaction and impossible to work with the sample during the fusion. Burners are used often as a convenient heat source although they make it difficult to heat the sample evenly.

The maximum temperature employed varies considerably and depends on the sample and the flux. In order to minimize attack of the crucible and decomposition of the flux, excessive temperatures should be avoided. Once the salt has melted, the melt is swirled gently to monitor the reaction. The fusion continues until visible signs of reaction are completed (e.g., formation of gases, foaming, fumes). It is frequently difficult to decide when heating should be discontinued. In ideal cases, a clear melt serves to indicate the completeness of sample decomposition. In other cases, it is not as obvious, and the analyst must base the heating time on past experience with the sample type.

The melt is swirled during cooling to spread it over the inside of the crucible. Thin layers of salt on the sides of the crucible often will crack and flake into small pieces during cooling. These small fragments are easier to dissolve.

After the sample has returned to room temperature, the fused material is dissolved. The solvent is usually warm water or a dilute acid solution, depending on the salt. For example, dilute acid typically would not be used to dissolve a carbonate fusion because of losses to spray caused by release of CO_2. The aqueous solution from the dissolution of the fusion melt should be examined carefully for particles of undissolved sample. If undissolved particles are present, they should be separated from solution by centrifugation or filtration, and a second fusion should be performed.

Several types of materials are used for crucibles, but platinum, other metals (Ni, Zr, Ag), and graphite are most common. Graphite crucibles are a cost-effective alternative to metal crucibles; they are disposable, which eliminates the need for cleaning and the possibility of cross-sample contamination. Graphite crucibles are chemically inert and heat-resistant, although they do oxidize slowly at temperatures above 430 °C. Graphite is not recommended for extremely lengthy fusions or for reactions where the sample may be reduced. Platinum is probably the most commonly used crucible material. It is virtually unaffected by any of the usual acids, including hydrofluoric, and it is attacked only by concentrated phosphoric acid at very high temperatures, and by sodium carbonate. However, it dissolves readily in mixtures of hydrochloric and nitric acids (aqua regia), nitric acid containing added chlorides, or chlorine water or bromine water.

Platinum offers adequate resistance toward molten alkali metal, borates, fluorides, nitrates, and bisulfates. When using a platinum crucible, one should avoid using aqua regia, sodium peroxide, free elements (C, P, S, Ag, Bi, Cu, Pb, Zn, Se, and Te), ammonium, chlorine and volatile chlorides, sulfur dioxide, and gases with carbon content. Platinum crucibles can be cleaned in boiling HCl, by hand cleaning with sea sand, or by performing a blank fusion with sodium hydrogen sulfate.

Many kinds of salts are used for fusions. The lowest melting flux capable of reacting completely with the sample is usually the optimum choice. Basic fluxes, such as the carbonates, the hydroxides, and the borates, are used to attack acidic materials. Sodium or potassium nitrate may be added to furnish an oxidizing agent when one is needed, as with the sulfides, certain oxides, ferroalloys, and some silicate materials. The most effective alkaline oxidizing flux is sodium peroxide; it is both a strong base and a powerful oxidizing agent. Because it is such a strong alkali, sodium peroxide is often used even when no oxidant is required. Alternatively, acid fluxes are the pyrosulfates, the acid fluorides, and boric acids. Table 13.1 lists several types of fusions, examples of salts used for each type of fusion, and the melting points of the salts.

SULFATE FUSION is useful for the conversion of ignited oxides to sulfates, but is generally an ineffective approach for silicates. Sulfate fusion is particularly useful for BeO, Fe_2O_3, Cr_2O_3, MoO_3, TeO_2, TiO_2, ZrO_2, Nb_2O_5, Ta_2O_5, PuO_2, and rare earth oxides (Bock, 1979, pp. 77-82). Pyrosulfate fusions are prepared routinely in the laboratory by heating a mixture of sodium or potassium sulfate with a stoichiometric excess of sulfuric acid:

$$Na_2SO_4 + H_2SO_4 \rightarrow [2NaHSO_4] \rightarrow Na_2S_2O_7 + H_2O$$

$$Na_2S_2O_7 \rightarrow Na_2SO_4 + SO_3\uparrow$$

$$Na_2SO_4 \text{ etc.}$$

The rate of heating is increased with time until the sulfuric acid has volatilized and a clear pyrosulfate fusion is obtained. It is important to note that pyrosulfate fusions are reversible and, if needed, the fusion can be cooled, additional sulfuric acid added, and the fusion repeated as many times as needed to dissolve the sample. The analyst must distinguish between insoluble material that has not yet or will not dissolve, and material that has precipitated during the final stages of a prolonged pyrosulfate fusion. In the latter situation the fusion must be cooled, additional sulfuric acid added, and the sample refused until the precipitated material redissolves and a clear melt is obtained. Otherwise, the precipitated material will be extremely difficult, if not impossible, to dissolve in subsequent steps. Platinum or quartz crucibles are recommended

for this type of fusion, with quartz being preferred for analysis of the platinum group metals. After the melt is cooled and solidified, it should be dissolved in dilute sulfuric or hydrochloric acid rather than in water to avoid hydrolysis and precipitation of Ti, Zr, etc. Niobium and tantalum may precipitate even in the presence of more concentrated acid. In order to avoid precipitation of Nb or Ta, concentrated sulfuric acid, tartaric acid, ammonium oxalate, hydrogen peroxide, or hydrofluoric acid must be used. Mercury and the anions of volatile acids are largely volatilized during these fusion procedures.

13.3.1 Alkali-Metal Hydroxide Fusions

Alkali metal hydroxide fusions are used for silicate analysis of ash and slag; for decomposition of oxides, phosphates, and fluorides (Bock, 1979, pp. 102-108); and for dissolution of soils for actinide analyses (Smith et al., 1995). Sodium hydroxide (NaOH) generally is used because of its lower melting point, but potassium hydroxide (KOH) is just as effective. These fusions generally are rapid, the melts are easy to dissolve in water, and the losses because of volatility are reduced because of the low temperature of the melt. Nickel, silver, or glassy carbon crucibles are recommended for this type of fusion. The maximum suggested temperature for nickel crucibles is 600 °C, but silver crucibles can be used up to 700 °C. Generally, crucibles made of platinum, palladium, and their alloys should not be used with hydroxide fusions because the crucibles are easily attacked in the presence of atmospheric oxygen. The weight ratio of fusion salt to sample is normally 5-10:1. Typically, these fusions are carried out below red heat at 450 to 500 °C for 15 to 20 minutes, or sometimes at higher temperatures between 600 to 700 °C for 5 to 10 minutes. The solidified melt dissolves readily in water; and therefore, this step may be carried out directly in the crucible, or alternatively in a nickel dish. Under no circumstances should the dissolution be carried out in a glass vessel because the resulting concentrated hydroxide solution attacks glass quite readily.

FUSION WITH SODIUM CARBONATE (Na_2CO_3) is a common procedure for decomposing silicates (clays, rocks, mineral, slags, glasses, etc.), refractory oxides (magnesia, alumina, beryllia, zirconia, quartz, etc.), and insoluble phosphates and sulfates (Bogen, 1978). The fusion may result in the formation of a specific compound such as sodium aluminate, or it may simply convert a refractory oxide into a condition where it is soluble in hydrochloric acid—this is the method of choice when silica in a silicate is to be determined, because the fusion converts an insoluble silicate into a mixture that is easily decomposed by hydrochloric acid ("M" represents a metal in the equations below):

$$MSiO_3 + Na_2CO_3 \rightarrow Na_2SiO_3 + MCO_3 \text{ (or } MO + CO_2),$$

followed by acidification to form a more soluble chloride salt,

$$Na_2SiO_3 + MCO_3 + 4\,HCl + x\,H_2O \rightarrow H_2SiO_3 \cdot x\,H_2O + MCl_2 + CO_2 + H_2O + NaCl.$$

Carbonate fusions provide an oxidizing melt for the analysis of chromium, manganese, sulfur, boron, and the platinum group metals. Organic material is destroyed, sometimes violently. Na_2CO_3 generally is used because of its lower melting point. However, despite its higher melting point and hygroscopic nature, K_2CO_3 is preferred for niobium and tantalum analyses because the resulting potassium salts are soluble, whereas the analogous sodium salts are insoluble.

The required temperature and duration of the fusion depend on the nature of the sample as well as particle size. In the typical carbonate fusion, 1 g of the powdered sample is mixed with 4 to 6 g of sodium carbonate and heated at 900 to 1,000 °C for 10 to 30 minutes. Very refractory materials may require heating at 1,200 °C for as long as 1 to 2 hours. Silica will begin to react at 500 °C, while barium sulfate and alumina react at temperatures above 700 °C. Notably, volatility is a problem at these temperatures. Mercury and thallium are lost completely, while selenium, arsenic, and iodine suffer considerable losses. Non-silicate samples should be dissolved in water, while silicate samples should be treated with acid (Bock, 1979, p. 111).

Platinum crucibles are recommended, even though there is a 1 to 2 mg loss of platinum per fusion. Attack on the crucible can be reduced significantly by covering the melt with a lid during the fusion process, or virtually eliminated by working in an inert atmosphere. Moreover, nitrate is often added to prevent the reduction of metals and the subsequent alloying with the platinum crucibles. The platinum crucibles may be seriously attacked by samples containing high concentrations of Fe^{2+}, Fe^{3+}, Sn^{4+}, Pb^{2+}, and compounds of Sb and As, because these ions are reduced easily to the metallic state and then form intermetallic alloys with platinum that are not easily dissolved in mineral acids. This problem is especially prevalent when fusion is carried out in a gas flame. Porcelain crucibles are corroded rapidly and should be discarded after a single use.

13.3.2 Boron Fusions

Fusions with boron compounds are recommended for analysis of sand, slag, aluminum silicates, alumina (Al_2O_3), iron and rare earth ores, zirconium dioxide, titanium, niobium, and tantalum. Relatively large amounts of flux are required for these types of fusions. The melts are quite viscous and require swirling or stirring, so they should not be performed in a furnace. Platinum crucibles should be used for these fusions because other materials are rapidly attacked by the melt, even though some platinum is lost in each fusion.

352 BORIC ACID (H_3BO_3) can be used to fuse a number of otherwise rather inert substances such as
353 sand, aluminum silicates, titanite, natural aluminum oxide (corundum), and enamels. Boric acid
354 fusions generally require 4 to 8 times as much reagent as sample. Initially, the mixture should be
355 heated cautiously while water is being driven off, then more strongly until gas evolution is
356 completed, and then more vigorously if the sample has yet to be fully decomposed. Normally, the
357 procedure is complete within 20 to 30 minutes. The cooled and solidified melt usually is
358 dissolved in dilute acid. Additionally, boric acid has one great advantage over all other fluxes in
359 that it can be completely removed by addition of methanol and subsequent volatilization of the
360 methyl ester.

361 Because MOLTEN SODIUM TETRABORATE ($Na_2B_4O_7$) dissolves so many inorganic compounds, it is
362 an important analytical tool for dissolving very resistant substances. Fusions with sodium
363 tetraborate alone are useful for Al_2O_3, ZrO_2 and zirconium ores, minerals of the rare earths,
364 titanium, niobium, and tantalum, aluminum-containing materials, and iron ores and slags (Bock,
365 1979). Relatively large amounts of borax are mixed with the sample, and the fusion is carried out
366 at a relatively high temperature (1,000 to 1,200 °C) until the melt becomes clear. Thallium,
367 mercury, selenium, arsenic, and the halogens are volatilized under these conditions. Boric acid
368 can be removed from the melt as previously described. By dissolving the melt in dilute
369 hydrofluoric acid, calcium, thorium, and the rare earths can be separated from titanium, niobium,
370 and tantalum as insoluble fluorides.

371 Fluxes of LITHIUM TETRABORATE ($Li_2B_4O_7$) are well suited for dissolving basic oxides such as
372 alumina (SiO_2) and some resistant silicates. However, lithium metaborate, $LiBO_2$, (or a mixture
373 of meta- and tetraborate) is more basic and better suited for dissolving acidic oxides such as
374 silica or titanium dioxide, although it is capable of dissolving nearly all minerals (Dean, 1995).
375 Platinum dishes normally are used for this type of fusion, but occasionally graphite crucibles are
376 advantageous because they can be heated rapidly by induction heating and because they are not
377 wetted by $Li_2B_4O_7$ melts. The fusion melt typically is dissolved in dilute acid, usually nitric but
378 sometimes sulfuric. When easily hydrolyzed metal ions are present, it is recommended that
379 dissolution be carried out in the presence of EDTA or its sodium salt in 0.01 M HCl (Bock, 1979,
380 p. 92). Moreover, when titanium is present, hydrogen peroxide can be used to help maintain the
381 titanium in solution.

382 ### 13.3.3 Fluoride Fusions

383 Fluoride fusions are used for the removal of silicon, the destruction of silicates and rare earth
384 minerals, and the analysis of oxides of niobium, tantalum, titanium, and zirconium. Sill et al.
385 (1974) and Sill and Sill (1995) has described a method using potassium fluoride/potassium

pyrosulfate fusion for determining alpha-emitting nuclides in soil (see Sect. 13.8). Sulcek and Povondra (1989) describe the isolation of the rare earth elements (REE) and thorium from silicate materials and their minerals, especially monazite, through potassium hydrofluoride fusion. The silicate matrix is first degraded by evaporation with HF, then the residue is fused with tenfold excess flux, and finally the melt is digested with dilute acid. The resulting fluorides (REE + Th + Ca + U) are filtered off, dissolved, and further separated by chromatography.

Platinum crucibles are recommended for fluoride fusions. Silicon and boron are volatilized during these fusion procedures, and if the temperature is high enough, some molybdenum, tantalum, and niobium also are lost. Residual fluoride can be a problem for subsequent analysis of many elements such as aluminum, tin, beryllium, and zirconium. This excess fluoride usually is removed by evaporation with sulfuric acid.

13.4 Wet Ashing and Acid Dissolution Techniques

"Wet ashing" and "acid dissolution" are terms used to describe sample decomposition using hot, concentrated acid solutions. Because many inorganic matrices such as oxides, silicates, nitrides, carbides, and borides can be difficult to dissolve completely, geological or ceramic samples can be particularly challenging. Therefore, different acids are used alone or in combination to decompose specific compounds that may be present in the sample. Few techniques will completely decompose all types of samples. Many decomposition procedures use wet ashing to dissolve the major portion of the sample but leave a minor fraction as residue. Whether or not this residue requires additional treatment (by wet ashing or fusion) depends on the amount of residue and whether it is expected to contain the radionuclides of interest. The residue should not be discarded until all of the results have been reviewed and determined to be acceptable.

13.4.1 Acids and Oxidants

Numerous acids are commonly used in wet ashing procedures. Table 13.2 lists several acids and the types of compounds they generally react with during acid dissolution. The electromotive force series (Table 13.3) is a summary of oxidation-reduction half-reactions arranged in decreasing oxidation strength and is also useful in selecting reagent systems (Dean, 1995). The table allows one to predict which metals will dissolve in nonoxidizing acids, such as hydrochloric, hydrobromic, hydrofluoric, phosphoric, dilute sulfuric, and dilute perchloric acid The dissolution process is simply a replacement of hydrogen by the metal (Dean, 1995). In practice, however, what actually occurs is influenced by a number of factors, and the behavior of the metals cannot be predicted from the potentials alone. Generally, metals below hydrogen in Table 13.3 displace hydrogen and dissolve in nonoxidizing acids with the evolution of hydrogen.

Notable exceptions include the very slow dissolution by hydrochloric acid of lead, cobalt, nickel, cadmium, and chromium. Also, lead is insoluble in sulfuric acid because of the formation of a surface film of insoluble lead sulfate.

TABLE 13.2 — Examples of acids used for wet ashing

Acid	Typical Uses
Hydrofluoric Acid, HF	Removal of silicon and destruction of silicates; dissolves oxides of Nb, Ta, Ti, and Zr, and Nb, and Ta ores.
Hydrochloric Acid, HCl	Dissolves many carbonates, oxides, hydroxides, phosphates, borates, and sulfides; dissolves cement.
Hydrobromic Acid, HBr	Distillation of bromides (e.g., As, Sb, Sn, Se).
Hydroiodic Acid, HI	Effective reducing agent; dissolves Sn (IV) oxide and Hg (II) sulfide.
Sulfuric Acid, H_2SO_4	Dissolves oxides, hydroxides, carbonates, and various sulfide ores; hot concentrated acid will oxidize most organic compounds.
Phosphoric Acid, H_3PO_4	Dissolves Al_2O_3, chrome ores, iron oxide ores, and slag.
Nitric Acid, HNO_3	Oxidizes many metals and alloys to soluble nitrates; organic material oxidized slowly.
Perchloric Acid, $HClO_4$	Extremely strong oxidizer; reacts violently or explosively to oxidize organic compounds; attacks nearly all metals.

TABLE 13.3 — Standard reduction potentials of selected half-reactions at 25 °C

Half-Reaction	E^0 (volts)
$Ag^{2+} + e^- = Ag^+$	1.980
$S_2O_8^{2-} + 2e^- = 2SO_4^{2-}$	1.96
$HN_3 + 3H^+ + 2e^- = NH_4^+ + N_2$	1.96
$Ce^{4+} + e^- = Ce^{3+}$	1.72
$MnO_4^- + 4H^+ + 3e^- = MnO_2\,(c) + 2H_2O$	1.70
$2HClO + 2H^+ + 2e^- = Cl_2 + 2H_2O$	1.630
$2HBrO + 2H^+ + 2e^- = Br_2 + 2H_2O$	1.604
$NiO_2 + 4H^+ + 2e^- = Ni^{2+} + 2H_2O$	1.593
Bi_2O_4 (bismuthate) $+ 4H^+ + 2e^- = 2BiO^+ + 2H_2O$	1.59
$MnO_4^- + 8H^+ + 5e^- = Mn^{2+} + 4H_2O$	1.51
$2BrO_3^- + 12H^+ + 10e^- = Br_2 + 6H_2O$	1.478
$PbO_2 + 4H^+ + 2e^- = Pb^{2+} + 2H_2O$	1.468
$Cr_2O_7^{2-} + 14H^+ + 6e^- = 2Cr^{3+} + 7H_2O$	1.36
$Cl_2 + 2e^- = 2Cl^-$	1.3583
$2HNO_2 + 4H^+ + 4e^- = N_2O + 3H_2O$	1.297

	Half-Reaction	E^0 (volts)
450	$MnO_2 + 4H^+ + 2e^- = Mn^{2+} + 2H_2O$	1.23
451	$O_2 + 4H^+ + 4e^- = 2H_2O$	1.229
452	$ClO_4^- + 2H^+ + 2e^- = ClO_3^- + H_2O$	1.201
453	$2IO_3^- + 12H^+ + 10e^- = I_2 + 3H_2O$	1.195
454	$N_2O_4 + 2H^+ + 2e^- = 2HNO_3$	1.07
455	$2ICl_2^- + 2e^- = 4Cl^- + I_2$	1.07
456	Br_2 (lq) $+ 2e^- = 2Br^-$	1.065
457	$N_2O_4 + 4H^+ + 4e^- = 2NO + 2H_2O$	1.039
458	$HNO_2 + H^+ + e^- = NO + H_2O$	0.996
459	$NO_3^- + 4H^+ + 3e^- = NO + 2H_2O$	0.957
460	$NO_3^- + 3H^+ + 2e^- = HNO_2 + H_2O$	0.94
461	$2Hg^{2+} + 2e^- = Hg_2^{2+}$	0.911
462	$Cu^{2+} + I^- + e^- = CuI$	0.861
463	OsO_4 (c) $+ 8H^+ + 8e^- = Os + 4H_2O$	0.84
464	$Ag^+ + e^- = Ag$	0.7991
465	$Hg_2^{2+} + 2e^- = 2Hg$	0.7960
466	$Fe^{3+} + e^- = Fe^{2+}$	0.771
467	$H_2SeO_3 + 4H^+ + 4e^- = Se + 3H_2O$	0.739
468	$HN_3 + 11H^+ + 8e^- = 2NH_4^+$	0.695
469	$O_2 + 2H^+ + 2e^- = H_2O_2$	0.695
470	$Ag_2SO_4 + 2e^- = 2Ag + SO_4^{2-}$	0.654
471	$Cu^{2+} + Br^- + e^- = CuBr$ (c)	0.654
472	$2HgCl_2 + 2e^- = Hg_2Cl_2$ (c) $+ 2Cl^-$	0.63
473	$Sb_2O_5 + 6H^+ + 4e^- = 2SbO^+ + 3H_2O$	0.605
474	$H_3AsO_4 + 2H^+ + 2e^- = HAsO_2 + 2\,H_2O$	0.560
475	$TeOOH^+ + 3H^+ + 4e^- = Te + 2H_2O$	0.559
476	$Cu^{2+} + Cl^- + e^- = CuCl$ (c)	0.559
477	$I_2^- + 2e^- = 3I^-$	0.536
478	$I_2 + 2e^- = 2I^-$	0.536
479	$Cu^+ + e^- = Cu$	0.53
480	$4H_2SO_3 + 4H^+ + 6e^- = S_4O_6^{2-} + 6H_2O$	0.507
481	$Ag_2CrO_4 + 2e^- = 2Ag + CrO_4^{2-}$	0.449
482	$2H_2SO_3 + 2H^+ + 4e^- = S_2O_3^{2-} + 3H_2O$	0.400
483	$UO_2^+ + 4H^+ + e^- = U^{4+} + 2H_2O$	0.38
484	$Cu^{2+} + 2e^- = Cu$	0.340
485	$VO^{2+} + 2H^+ + e^- = V^{3+} + H_2O$	0.337
486	$BiO^+ + 2H^+ + 3e^- = Bi + H_2O$	0.32
487	$UO_2^{2+} + 4H^+ + 2e^- = U^{4+} + 2H_2O$	0.27
488	Hg_2Cl_2 (c) $+ 2e^- = 2Hg + 2Cl^-$	0.2676

Half-Reaction	E^0 (volts)
$AgCl + e^- = Ag + Cl^-$	0.2223
$SbO^+ + 2H^+ + 3e^- = Sb + H_2O$	0.212
$CuCl_3^{2-} + e^- = Cu + 3Cl^-$	0.178
$SO_4^{2-} + 4H^+ + 2e^- = H_2SO_3 + H_2O$	0.158
$Sn^{4+} + 2e^- = Sn^{2+}$	0.15
$CuCl + e^- = Cu + Cl^-$	0.121
$TiO^{2+} + 2H^+ + e^- = Ti^{3+} + H_2O$	0.100
$S_4O_6^{2-} + 2e^- = 2S_2O_3^{2-}$	0.08
$2H^+ + 2e^- = H_2$	0.0000
$Hg_2I_2 + 2e^- = 2Hg + 2I^-$	-0.0405
$Pb^{2+} + 2e^- = Pb$	-0.125
$Sn^{2+} + 2e^- = Sn$	-0.136
$AgI + e^- = Ag + I^-$	-0.1522
$V^{3+} + e^- = V^{2+}$	-0.255
$Ni^{2+} + 2e^- = Ni$	-0.257
$Co^{2+} + 2e^- = Co$	-0.277
$PbSO_4 + 2e^- = Pb + SO_4^{2-}$	-0.3505
$Cd^{2+} + 2e^- = Cd$	-0.4025
$Cr^{3+} + e^- = Cr^{2+}$	-0.424
$Fe^{2+} + 2e^- = Fe$	-0.44
$H_3PO_3 + 2H^+ + 2e^- = HPH_2O_2 + H_2O$	-0.499
$U^{4+} + e^- = U^{3+}$	-0.52
$Zn^{2+} + 2e^- = Zn$	-0.7626
$Mn^{2+} + 2e^- = Mn$	-1.18
$Al^{3+} + 3e^- = Al$	-1.67
$Mg^{2+} + 2e^- = Mg$	-2.356
$Na^+ + e^- = Na$	-2.714
$K^+ + e^- = K$	-2.925
$Li^+ + e^- = Li$	-3.045

Source: Dean, 1995.

Oxidizing acids, such as nitric acid, hot concentrated sulfuric acid, or hot concentrated perchloric acid, are used to dissolve metals above hydrogen. For nitric acid, the potential of the nitrate ion-nitric oxide couple can be employed as a rough estimate of the solvent power. For aqua regia, the presence of free chlorine ions allows one to make predictions based upon the potential of the chlorine-chloride couple, although NOCl also plays a significant role. Some oxidizing acids exhibit a passivating effect with transition elements such as chromium and pure tungsten, resulting in a very slow attack because of the formation of an insoluble surface film of the oxide

in the acid (Bogen, 1978). Moreover, oxides are often resistant to dissolution in oxidizing acids and, in fact, dissolve much more readily in nonoxidizing acids. A common example is ferric oxide, which is readily soluble in hydrochloric acid but is relatively inert in nitric acid.

However, insoluble oxides of the lower oxidation states of an element sometime dissolve in oxidizing acids with concurrent oxidation of the element. For example, UO_2 and U_3O_8 dissolve readily in nitric acid to produce a solution of uranyl ion (UO_2^{+2}).

HYDROFLUORIC ACID. The most important property of HF is its ability to dissolve silica and other silicates. For example:

$$SiO_2 + 6HF \rightarrow H_2SiF_6 + 2H_2O$$

whereby the fluorosilicic acid formed dissociates into gaseous silicon tetrafluoride and hydrogen fluoride upon heating:

$$H_2SiF_6 \rightarrow SiF_4\uparrow + 2HF$$

HF also exhibits pronounced complexing properties that are widely used in analytical chemistry. Hydrofluoric acid prevents the formation of sparingly soluble hydrolytic products in solution, especially of compounds of elements from the IVth to VIth groups of the periodic table (Sulcek and Povondra, 1989). In the presence of fluoride, soluble hydrolytic products that are often polymeric depolymerize to form reactive monomeric species suitable for further analytical operations. Formation of colloidal solutions is avoided and the stability of solutions is increased even with compounds of elements that are hydrolyzed easily in aqueous solution (e.g., Si, Sn, Ti, Zr, Hf, Nb, Ta, and Pa).

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HF should never be used or stored in glass containers. Platinum containers are preferred, and Teflon is acceptable as long as the temperature does not exceed 250 °C; the constant boiling

azeotrope boils at 112 °C. HF works most effectively when used alone. Samples should be ground to a fine powder to increase the surface area and moistened with water to prevent losses as dust and spray when the acid is added to the sample. After the addition of HF, the sample is allowed to stand overnight to dissolve the silicates. However, the reaction can be sped up by heating the solution. Because it is such a strong complexing agent, excess fluoride ion can cause problems with many chemical reactions. Residual fluoride is usually removed by evaporation to fumes in a low-volatility acid (e.g., H_2SO_4, HNO_3, $HClO_4$) or, in extreme cases, excess fluoride ion can be removed by fusing the residue with $K_2S_2O_7$ or by the addition of quartz (SiO_2).

HYDROCHLORIC ACID (HCl) is one of the most widely used acids for wet ashing samples because of the wide range of compounds it reacts with and the low boiling point of the azeotrope (110 °C); after a period of heating in an open container, a constant boiling 6M solution remains. HCl forms strong complexes with gold (III), titanium (III), and mercury (II). The concentrated acid will also complex iron (III), gallium (III), indium (III), and tin (IV). Most chloride compounds are readily soluble in water except for silver chloride, mercury chloride, titanium chloride, and lead chloride. HCl can be oxidized to form chlorine gas by manganese dioxide, permanganate, and persulfate. While HCl dissolves many carbonates, oxides, hydroxides, phosphates, borates, sulfides, and cement, it does not dissolve the following:

- Most silicates or ignited oxides of Al, Be, Cr, Fe, Ti, Zr, or Th;
- Oxides of Sn, Sb, Nb, or Ta;
- Zr phosphate;
- Sulfates of Sr, Ba, Ra, or Pb;
- Alkaline earth fluorides;
- Sulfides of Hg; or
- Ores of Nb, Ta, U, or Th.

The dissolution behavior of specific actinides by hydrochloric acid is discussed by Sulcek and Povondra (1989):

> "The rate of decomposition of oxidic uranium ores depends on the U(VI)/U(IV) ratio. The so-called uranium blacks with minimal contents of U(IV) are even dissolved in dilute hydrochloric acid. Uraninite (UO_2) requires an oxidizing mixture of hydrochloric acid with hydrogen peroxide, chlorate, or nitric acid for dissolution. Uranium and thorium compounds cannot be completely leached from granites by hydrochloric acid. Natural and synthetic thorium dioxides are highly resistant toward hydrochloric acid and must be decomposed in a pressure vessel. Binary phosphates of uranyl and divalent cations, e.g., autunite and tobernite, are dissolved without difficulties. On the other hand, phosphates of thorium, tetravalent

uranium, and the rare earths (monazite and xenotime) are only negligibly attacked, even with the concentrated acid."

Arsenic (III), antimony (III), germanium (III), and selenium (IV) are easily volatilized in HCl solutions, while mercury (II), tin (IV), and rhenium (VII) are volatilized in the latter stages of evaporation. Glass is the preferred container for HCl solutions.

HYDROBROMIC ACID (HBr) has no important advantages over HCl for wet ashing samples. HBr forms an azeotrope with water containing 47.6 percent w/w of HBr, boiling at 124.3 °C. HBr is used to distill off volatile bromides of arsenic, antimony, tin, and selenium. HBr can also be used as a complexing agent for liquid-liquid extractions of gold, titanium, and indium.

HYDROIODIC ACID (HI) is readily oxidized and often appears as a yellowish-brown liquid because of free iodine. HI is most often used as a reducing agent during dissolutions. HI also dissolves tin (IV) oxide, and complexes and dissolves mercury (II) sulfide. HI forms an azeotrope with water containing 56.9 percent w/w of HI, boiling at 127 °C.

SULFURIC ACID (H_2SO_4) is another widely used acid for sample decomposition. Part of its effectiveness is due to its high boiling point (about 340 °C). Oxides, hydroxides, carbonates, and sulfide ores can be dissolved in H_2SO_4. The boiling point can be raised by the addition of sodium or potassium sulfate to improve the attack on ignited oxides, although silicates will still not dissolve. H_2SO_4 is not appropriate when calcium is a major constituent because of the low solubility of $CaSO_4$. Other inorganic sulfates are typically soluble in water, with the notable exceptions of strontium, barium, radium, and lead.

Dilute H_2SO_4 does not exhibit oxidizing properties, but the concentrated acid will oxidize many elements and almost all organic compounds. Oxidation of organic compounds in H_2SO_4 is a slow reaction with a tendency to form indestructible charred residues. Moreover, because of the high boiling point of H_2SO_4, there is an increased risk of losses because of volatilization. Iodine can be distilled quantitatively, and boron, mercury, selenium, osmium, ruthenium, and rhenium may be lost to some extent. The method of choice is to oxidize the organic substances with HNO_3, volatilize the nitric acid, add H_2SO_4 until charred, followed by HNO_3 again, repeating the process until the sample will not char with either HNO_3 or H_2SO_4. Dissolution is then continued with $HClO_4$.

Glass, quartz, platinum, and porcelain are resistant to H_2SO_4 up to the boiling point. Teflon decomposes at 300 °C, below the boiling point, and, therefore, is not recommended for applications involving H_2SO_4 that require elevated temperature.

PHOSPHORIC ACID (H_3PO_4) seldom is used for wet ashing because the residual phosphates interfere with many procedures. H_3PO_4 attacks glass, although glass containers are usually acceptable at temperatures below 300 °C. Alumina, chromium ores, iron oxide ores, and slags can be dissolved in H_3PO_4. The acid also has been used to dissolve silicates selectively without attacking quartz.

NITRIC ACID (HNO_3) is one of the most widely used oxidizing acids for sample decomposition. Most metals and alloys are oxidized to nitrates, which are usually very soluble in water, although many metals exhibit a pronounced tendency to hydrolyze in nitric acid solution. Nitric acid does not attack gold, hafnium, tantalum, zirconium, and the metals of the platinum group (except palladium). Aluminum, boron, chromium, gallium, indium, niobium, thorium, titanium, calcium, magnesium, and iron form a layer of insoluble oxide when treated with HNO_3 and are thereby pacified and do not dissolve in the concentrated acid. However, calcium, magnesium, and iron will dissolve in more dilute acid.

Complexing agents (e.g., Cl^-, F^-, citrate, tartrate) can assist HNO_3 in dissolving most metals. For example, Sulcek and Povondra (1989) describe the decomposition of thorium and uranium dioxides in nitric acid, which is catalytically accelerated by the addition of 0.05 to 0.1 M HF. They report that a solid solution of the mixed oxides (Pu, U)O_2 or PuO_2 ignited at temperatures below 800 °C behaves analogously.

Although nitric acid is a good oxidizing agent, it usually boils away before sample oxidation is complete. Oxidation of organic materials proceeds slowly and is usually accomplished by repeatedly heating the solution to HNO_3 fumes. Refluxing in the concentrated acid can help facilitate the treatment, but HNO_3 is seldom used alone to decompose organic materials.

PERCHLORIC ACID ($HClO_4$). Hot concentrated solutions of $HClO_4$ act as a powerful oxidizer, but dilute aqueous solutions are not oxidizing. Hot concentrated $HClO_4$ will attack nearly all metals (except gold and platinum group metals) and oxidize them to the highest oxidation state, except for lead and manganese, which are oxidized only to the +2 oxidation state. Perchloric acid is an excellent solvent for stainless steel, oxidizing the chromium and vanadium to the hexavalent and pentavalent acids, respectively. Many nonmetals also will react with $HClO_4$. Because of the violence of the oxidation reactions, $HClO_4$ is rarely used alone for the destruction of organic materials. H_2SO_4 or HNO_3 are used to dilute the solution and break down easily oxidized material before $HClO_4$ becomes an oxidizer above 160 °C.

The concentrated acid is a dangerous oxidant that can explode violently. The following are examples of some reactions with $HClO_4$ that *should never be attempted*:

- Heating Bi metal and alloys with concentrated acid.
- Dissolving metals (e.g., steel) in concentrated acid when gas-phase hydrogen becomes heated.
- Heating uranium turnings or powder in concentrated acid.
- Heating finely divided aluminum and silicon in concentrated acid.
- Heating antimony or antimony (III) compounds in $HClO_4$.
- Mixing $HClO_4$ with hydrazine or hydroxylamine.
- Mixing $HClO_4$ with hypophosphates.
- Mixing $HClO_4$ with fats, oils, greases, or waxes.
- Evaporating solutions of metal salts to dryness in $HClO_4$.
- Evaporating alcoholic filtrates after collection of $KClO_4$ precipitates.
- Heating $HClO_4$ with cellulose, sugar, and polyhydroxy alcohols.
- Heating $HClO_4$ with N-heterocyclic compounds.
- Mixing $HClO_4$ with any dehydrating agent.

Perchloric acid vapor should never be allowed to come in contact with organic materials such as rubber stoppers. The acid should be stored only in glass bottles. Splashed or spilled acid should be diluted with water immediately and mopped up with a woolen cloth, never cotton. $HClO_4$ should only be used only in specially designed fume hoods incorporating a washdown system.

Acid dissolutions involving $HClO_4$ should only be performed by analysts experienced in working with this acid. When any procedure is designed, the experimental details should be recorded exactly. These records are used to develop a detailed SOP that must be followed exactly to ensure the safety of the analyst (Schilt, 1979).

AQUA REGIA. One part concentrated HNO_3 and 3 parts concentrated HCl (volume/volume) are combined to form aqua regia:

$$3HCl + HNO_3 \rightarrow NOCl + Cl_2 + 2H_2O$$

However, the interaction of these two acids is much more complex than indicated by this simple equation. Both the elemental chlorine and the trivalent nitrogen of the nitrosyl chloride exhibit oxidizing effects, as do other unstable products formed during the reaction of these two acids. Coupled with the catalytic effect of Cl_2 and NOCl, this mixture combines the acidity and complexing power of the chloride ions. The solution is more effective if allowed to stand for 10 to 20 minutes after it is prepared.

Aqua regia dissolves sulfides, phosphates, and many metals and alloys including gold, platinum, and palladium. Ammonium salts are decomposed in this acid mixture. Aqua regia volatilizes osmium as the tetroxide; has little effect on rhodium, iridium, and ruthenium; and has no effect on titanium. Oxidic uranium ores with uraninite and synthetic mixed oxides (U_3O_8) are dissolved in aqua regia, with oxidation of the uranium (VI) to UO_2^{2+} ions (Sulcek and Povondra, 1989). However, this dissolution procedure is insufficient for poor ores; the resistant, insoluble fraction must be further attacked (e.g., by sodium peroxide or borate fusion) or by mixed-acid digestion with HF, HNO_3, and $HClO_4$.

Oxysalts, such as $KMnO_4$ (potassium permanganate) and $K_2Cr_2O_7$ (potassium dichromate), are commonly not used to solubilize or wet ash environmental samples for radiochemical analysis because of their limited ability to oxidize metals and the residue that they leave in the sample mixture. These oxysalts are more commonly used to oxidize organic compounds.

POTASSIUM PERMANGANATE ($KMnO_4$) is a strong oxidizer whose use is limited primarily to the decomposition of organic substances and mixtures, although it oxidizes metals such as mercury to the ionic form. Oxidation can be performed in an acid, neutral, or basic medium; near-neutral or basic solutions produce an insoluble residue of manganese dioxide (MnO_2) that can be removed by filtration. Oxidation in acid media leaves the manganese (II) ion in solution, which might interfere with additional chemical procedures or analyses. Extreme caution must be taken when using this reagent because $KMnO_4$ reacts violently with some organic substances such as acetic acid and glycerol, with some metals such as antimony and arsenic, and with common laboratory reagents such as hydrochloric acid and hydrogen peroxide.

POTASSIUM DICHROMATE ($K_2Cr_2O_7$) is a strong oxidizing agent for organic compounds but is not as strong as $KMnO_4$. $K_2Cr_2O_7$ has been used to determine carbon and halogen in organic

materials, but the procedure is not used extensively. $K_2Cr_2O_7$ is commonly mixed with sulfuric acid and heated. The chromium (III) ion remains after sample oxidation and this might interfere with other chemical procedures or analyses. $K_2Cr_2O_7$ can react violently with certain organic substances such as ethanol and might ignite in the presence of boron. Caution also must be observed in handling this oxidizing agent because of human safety concerns, particularly with the hexavalent form of chromium.

SODIUM BROMATE ($NaBrO_3$) is an oxidizing agent for organic compounds but is not used for metals. Unlike $KMnO_4$ and $K_2Cr_2O_7$, the bromate ion can be removed from solution after sample oxidation by boiling with excess HCl to produce water and Br_2. Caution must be observed when using this oxidizing agent because it can react violently with some organic and inorganic substances.

13.4.2 Acid Digestion Bombs

Some materials that would not be totally dissolved by acid digestion in an open vessel on a hotplate, can be completely dissolved in an acid digestion bomb. These pressure vessels hold strong mineral acids or alkalies at temperatures well above normal boiling points, thereby allowing one to obtain complete digestion or dissolution of samples that would react slowly or incompletely at atmospheric pressure. Sample dissolution is obtained without losing volatile elements and without adding contaminants from the digestion vessel. Ores, rock samples, glass and other inorganic samples can be dissolved quickly using strong mineral acids such as HF, HCl, H_2SO_4, HNO_3, or aqua regia.

These sealed pressure vessels are lined with Teflon, which offers resistance to cross-contamination between samples and to attack by HF. In all reactions, the bomb must never be completely filled; there must be adequate vapor space above the contents. When working with inorganic materials, the total volume of sample plus reagents must never exceed two-thirds of the capacity of the bomb. Moreover, many organic materials can be treated satisfactorily in these bombs, but critical attention must be given to the nature of the sample as well to possible explosive reactions with the digestion media.

13.4.3 Is it Dissolved?

Following aggressive acid digestion and even fusion, the analyst often must determine if the sample has indeed been dissolved. This determination is first made through visual inspection for particulate matter in the acid leachate or dissolved fusion melt. If a residue is observed, this residue can be physically separated and subsequently fused or treated in an acid digestion bomb

to determine if any analyte was left behind. Sometimes these residues are inconsequential and contain no analyte of interest. In other cases, residues may consist of materials such as zircons or other minerals that can contain trapped uranium, thorium, etc. Even if no particles are readily observed, small undissolved particles that are invisible to the naked eye may be present. Therefore, the analyst may choose to filter the sample through a 0.22 to 0.45 μm filter, and then count the filter for gross α, β, and γ activity to determine if any activity has been left behind in the residue. However, this approach is applicable only for samples that contain elevated levels of radioactivity. Finally, for those cases where the laboratory has decided to perform an acid digestion rather than a total dissolution fusion, it is advisable to perform a total dissolution on a subset of the samples and compare the results to those obtained from the acid digestion. This check will help to substantiate that the acid digestion approach is adequate for the particular sample matrix.

13.5 Microwave Digestion

Microwave energy as a heat source for sample digestion was first described more than 20 years ago (Abu-Samra et al., 1975). Its popularity is derived from the fact that it is faster, cleaner, more reproducible, and more accurate than traditional hot-plate digestion. However, until recently, this technology has had limited application in the radiochemical laboratory because of constraints on sample size resulting from vessel pressure limitations. Because of this drawback, microwave dissolution was not practical for many radiochemical procedures where larger sample sizes are dictated to achieve required detection limits. However, recent advances in vessel design and improved detection methods, such as ICP-MS (inductively coupled plasma-mass spectrometry) and ion chromatography have eliminated this disadvantage, and microwave dissolution is becoming an important tool for today's radiochemists (Smith and Yaeger, 1996; Alvarado et al., 1996). A series of articles in the journal *Spectroscopy* describes recent advances in microwave dissolution technology (Kammin and Brandt, 1989; Grillo, 1989 and 1990; Gilman and Engelhardt, 1989; Lautenschlager, 1989; Noltner et al., 1990), and Dean (1995) presents a synopsis of current microwave theory and technology in the *Analytical Chemistry Handbook.* Moreover, *Introduction to Microwave Sample Preparation: Theory and Practice* by Kingston and Jassie (1988) and *Microwave-Enhanced Chemistry—Fundamentals, Sample Preparation, and Applications* by Kingston and Haswell (1997), are excellent resources for this topic.

Some example protocols for various media are given in ASTM standards: "Standard Practice for Acid-Extraction from Sediments Using Closed Vessel Microwave Heating" (ASTM D5258) describes the decomposition of soil and sediment samples for subsequent analyte extraction; "Standard Practice for Sample Digestion Using Closed Vessel Microwave Heating Technique for the Determination of Total Metals in Water" (ASTM D4309) addresses the decomposition of

surface, saline, domestic, and industrial waste water samples; and "Standard Practice for Microwave Digestion of Industrial Furnace Feedstreams for Trace Element Analysis" (ASTM D5513) covers the multistage decomposition of samples of cement raw feed materials, waste-derived fuels, and other industrial feedstreams for subsequent trace metal analysis. A method for acid digestion of siliceous and organically based matrices is given in EPA (1996).

There are various brands and models of microwave instruments that may be satisfactory depending on sample preparation considerations. The three main approaches to microwave dissolution are: focused open-vessel, low-pressure closed-vessel, and high-pressure closed-vessel. Each has certain advantages and disadvantages and the choice of system depends upon the application.

13.5.1 Focused Open-Vessel Systems

A focused open-vessel system has no oven but consists of a magnetron to generate microwaves, a waveguide to direct and focus the microwaves and a cavity to contain the sample (Grillo, 1989). Because of the open-vessel design, there is no pressure buildup during processing, and reagents may be added during the digestion program. These systems are quite universal in that any reagent and any type of vessel (glass, Perfluoroalcoholoxil™ [PFA], or quartz) can be used.

The waveguide ensures that energy is directed only at the portion of the vessel in the path of the focused microwaves thereby allowing the neck of the vessel and refluxer to remain cool and ensuring refluxing action. Because of this refluxing action, the system maintains all elements, even selenium and mercury. The focused microwaves cause solutions to reach higher temperatures faster than with conventional hotplates or block-type digesters and do so with superior reproducibility. An aspirator removes excess acid vapors and decomposition gases. Depending on the system, up to 20 g of solids or 50 to 100 mL of liquids can be digested within 10 to 30 minutes on average.

13.5.2 Low-Pressure, Closed-Vessel Systems

These systems consist of a microwave oven equipped with a turntable, a rotor to hold the sample vessels, and a pressure-control module (Grillo, 1990). The PFA vessels used with these systems are limited to approximately 225 °C, and, therefore, low-boiling reagents or mixtures of reagents should be used. However, waste is minimized in these systems because smaller quantities of acid are required. Moreover, because little or no acid is lost during the digestion, additional portions of acid may not be required and blank values are minimized. Additionally, these sealed vessels are limited to 100 to 300 psi, depending on the model thereby limiting the size of organic

808 samples utilized. However, inorganic materials such as metals, water and waste waters, minerals,
809 and most soils and sediments are easily digested without generating large amounts of gaseous by-
810 products. Typical sample sizes are on the order of 0.5 g for solids and 45 mL for waters.

811 The pressure control module regulates the digestion cycle by monitoring, controlling, and
812 dwelling at several preferred pressure levels for specified time periods in order to obtain
813 complete dissolution and precise recoveries in the minimum amount of time. As the samples are
814 irradiated, temperatures in the vessels rise thereby increasing the pressure. The pressure
815 transducer will cycle the magnetron to maintain sufficient heat to hold the samples at the
816 programmed pressure level for a preset dwell time. The vessels are designed to vent safely in
817 case of excessive internal pressure.

818 ### 13.5.3 High-Pressure, Closed-Vessel Systems

819 Recent advances in vessel design have produced microwave vessels capable of withstanding
820 pressures on the order of 1,500 psi (Lautenschlager, 1989), allowing for larger sample sizes on
821 the order of 1 to 2 g for soil (Smith and Yaeger, 1996) or 0.5 to 3 g for vegetation (Alvarado et
822 al., 1996) and, consequently, better detection limits. These high-pressure vessels are used to
823 digest organic and inorganic substances, such as coals, heavy oils, refractories, and ceramic
824 oxides, which cannot easily be digested with other techniques. Additionally, vessel composition
825 continues to improve. Noltner et al. (1990) have demonstrated that Tetrafluorometoxil™ (TFM)
826 vessels exhibit significantly lower blank background values from residual contamination and
827 reuse than vessels produced with the more traditional PFA. This lower "memory" results in lower
828 detection limits, a clear advantage for environmental laboratories.

829 ## 13.6 Special Matrix Considerations

830 ### 13.6.1 Liquid Samples

831 13.6.1.1 Aqueous Samples

832 Aqueous samples are usually considered to be in solution. This may not always be true, and,
833 based on the objectives of the project, additional decomposition of aqueous samples may be
834 requested.

835 13.6.1.2 Nonaqueous Samples

836 Most radiochemical analyses are performed in aqueous solutions. Because nonaqueous liquids
837 are incompatible with this requirement, these samples must be converted into an aqueous form.
838 In most cases, the nonaqueous liquid is simply a solvent that does not contain the radionuclide of
839 interest, and the nonaqueous solvent simply can be removed and the residue dissolved as
840 described in Sections 13.3 and 13.4.

841 Occasionally, the nonaqueous phase must be analyzed. A procedure for the decomposition of
842 petroleum products is described by Coomber (1975). There are restrictions on how many
843 nonaqueous liquids can be disposed of, even as laboratory samples. Evaporation of volatile
844 solvents may initially be an attractive alternative, but the legal restrictions on evaporating
845 solvents into the air should be investigated before this method is implemented. Burning flam-
846 mable liquids such as oil may also initially appear attractive, but legal restrictions on incineration
847 of organic liquids may need to be considered. A liquid-liquid extraction or separation using ion
848 exchange resin may be the only alternative for transferring the radionuclide of interest into an
849 aqueous solution. Unfortunately, these methods require extensive knowledge of the sample
850 matrix and chemical form of the contaminant, which is seldom available. Often, gross
851 radioactivity measurements using liquid scintillation counting techniques or broad spectrum
852 direct measurements such as gamma spectroscopy are the only measurements that can be
853 practically performed on nonaqueous liquids.

854 **13.6.2 Solid Samples**

855 Decomposition of solid samples is accomplished by applying fusion, wet ashing, leaching, or
856 combustion techniques singly or in some combination. A discussion of each of these techniques
857 is included in this chapter.

858 **13.6.3 Filters**

859 Air filter samples generally have a small amount of fine particulate material on a relatively small
860 amount of filter media. In many cases, filters of liquid samples also have limited amounts of
861 sample associated with the filter material. This situation may initially appear to make the sample
862 decomposition process much easier, the small amount of sample appears to dissolve readily in a
863 simple acid dissolution. The ease with which many filters dissolve in concentrated acid does not
864 always mean that the sample has dissolved, and the fine particles are often impossible to see in
865 an acid solution. If the radionuclides of concern are known to be in the oxide form, or if the
866 chemical form of the contaminants is unknown, a simple acid dissolution will not completely

dissolve the sample. In these cases, the sample may be dry ashed to destroy the filter and the residue subjected to fusion or other decomposition of oxides in the sample.

13.6.4 Wipe Samples

If oxides and silicates are not present in wipe samples, acid dissolutions are generally acceptable for sample decomposition. In many cases, it is not the sample but the material from which the wipe is constructed that causes problems with acid dissolution. Paper wipes are decomposed easily in sulfuric-nitric solutions or in perchloric nitric solutions or by combustion, and it may be necessary to dry ash the sample before dissolution. If volatile isotopes are expected, precautions must be taken to prevent loss when heating (see Section 14.5, "Volatilization and Distillation). "Sticky" smears can be more difficult to dissolve—the glue can be especially troublesome and should be watched closely if perchloric acid is used. Other materials used for wipe samples should be evaluated on an individual basis to determine the best method for sample decomposition. In some cases, the sample will be a problem to decompose as well. Oil and grease are often collected on wipe samples from machinery, and these samples are usually dry ashed before acid dissolution to remove the organic material. If large amounts of solid material (i.e., soil, dust, etc.) are collected with the wipe, it is recommended that the sample be treated as a solid (the analytical protocol specification or the project manager should be consulted before removing the wipe and simply analyzing the solid sample).

13.6.5 Liquid Scintillation Samples

Sample oxidation is used in association with liquid scintillation counting to enhance the solubility of samples, decolorize samples to limit quenching, separate radionuclides, concentrate the analyte from bulk material, or for a combination of these reasons.

13.6.5.1 Wet Oxidation

Wet oxidation reagents are used to liberate $^{14}CO_2$, $^{3}H_2O$, and $^{35}SO_3$ from samples containing ^{14}C, ^{3}H, and ^{35}S, respectively, with limited success (Gibbs et al., 1978; Peng, 1977). Nitric acid, nitric acid with perchloric acid, fuming sulfuric acid with periodate and chromic acid, and perchloric acid with hydrogen peroxide are employed. However, a consequence of using these strong reagents is the production of chemiluminescence. Moreover, these reagents also suppress counting efficiency because they are strong quenching agents.

13.6.5.2 Dry Oxidation

Dry oxidation refers to combustion of the sample in an oxygen atmosphere to yield the highest oxides, e.g., H_2O, CO_2, SO_3. Sample oxidizers are currently available for liquid scintillation based upon this approach. The current system uses a continuous flow of oxygen to ensure complete oxidation of the sample and to force the gaseous products through the H_2O and CO_2 collection regions and any untrapped gases to vented waste. The sample is loaded into a platinum-rhodium wire basket and then is sealed into the combustion flask. Oxygen begins to flow as an electric current passes through the wire basket to ignite the sample. The continuous flow of O_2 sweeps the gaseous combustion products into the air-cooled condenser. The collection of the combustion products consists of two consecutive stages. First, the water produced in the combustion process is condensed at 2 °C and collected. Second, the CO_2 produced in the combustion is isolated by a CO_2 absorber. Each fraction is then mixed with liquid scintillation cocktail and counted. This instrument is designed to give highly reproducible recoveries of ^3H and ^{14}C while eliminating chemiluminescence and various quenching problems.

13.7 Total Dissolution and Leaching

Sample dissolution can be one of the biggest challenges facing the analyst because the adequacy of the dissolution has direct and profound effects on the resultant data. The analyst must balance numerous factors such as the nature of the sample and the analyte (e.g., is it refractory or volatile?), the effects of excess reagents during subsequent analyses, the accuracy and precision requirements for the data, and the costs associated with effort, materials, and waste generation. Consequently, the question of total dissolution through fusion or digestion, or through acid leaching, is under constant debate, and it is important for the analyst to be aware of the limitations of both methods.

The MARLAP process enables one to make a decision concerning the dissolution required through its process of establishing data quality objectives, analytical protocol specification, and measurement quality objectives. During this process, all pertinent information is available to the radioanalytical specialist who then evaluates the alternatives and assists with the decision. The following discussion on acid leaching focuses on its use for the complete dissolution of the analyte of interest and not for such procedures as the Environmental Protection Agency's "Toxicity Characteristic Leaching Procedure" (TCLP; 40 CFR 261), which are intended to determine the leachability of a chemical.

13.7.1 Acid Leaching

"Acid leaching" has no accepted definition, but will be defined here as the use of nitric or hydrochloric acid to put the radionuclide into solution. The acid concentration may vary up to and include concentrated acid. Normally, the use of hydrofluoric acid and aqua regia are not included in this definition. Sample size is usually relatively much larger than that used for fusion. Although mineral acids might not totally break down all matrices, they have been shown to be effective leaching solvents for metals, oxides, and salts in some samples. In some cases, leaching requires fewer chemicals and less time to accomplish than complete sample dissolution. For matrices amenable to leaching, multiple samples are easily processed simultaneously using a hotplate or microwave system, and excess reagents can be removed through evaporation. Complete dissolution of a sample is not necessary if it can be demonstrated confidently that the radionuclide of interest is completely leached from the sample medium. However, if complete dissolution of the analyte cannot be so demonstrated, then it may be necessary to compare leaching data with data from totally dissolved samples in order for the analyst to determine the appropriate method for total analyte content of a specific set of samples. When leaching is a viable option for analyte removal, as an alternative to complete dissolution, the samples can be treated with strong acids to leach all or a large fraction of the radionuclides of interest from solid media. It may be possible to complete the dissolution of leach residue with hot aqua regia and then followed by hot hydrofluoric acid. The use of these acids is usually used on relatively small sample residues and may also be used on small samples.

Sill and Sill (1995) point out that:

> "In many cases, the mono-, di-, and small tervalent elements can be leached fairly completely from simple solids by boiling with concentrated hydrochloric or nitric acids. However, even these elements cannot necessarily be guaranteed to be dissolved completely by selective leaching. If they are included in a refractory matrix, they will not be removed completely without dissolution of the matrix. If the samples have been exposed to water over long periods of time, such as with sediments in a radioactive waste pond, small ions such as divalent cobalt will have diffused deeply into the rock lattice from which they cannot be removed without complete dissolution of the host matrix. In contrast, because of its large size, ionic cesium has a marked tendency to undergo isomorphous replacement in the lattice of complex silicates from which it too cannot be removed completely. In some unpublished work by the present authors, 15% of the ^{137}Cs and 5% of the ^{60}Co in some pond sediments remained in the residue after extensive leaching, and could not be removed by further boiling for two hours with either

concentrated nitric or hydrochloric acids. The fraction remaining in the residue was obviously much greater with shorter, more reasonable leaching times."

13.7.2 Total Dissolution through Fusion

There are those within the radiochemistry community who maintain that leaching techniques are always inadequate. Sill and Sill (1995), longtime proponents of total dissolution, state, "Any procedure that fails to obtain complete sample dissolution for whatever reasons of economy, speed, sample load, or other expediency is untrustworthy at best, and will inevitably give low and erratic results." They go on to support their argument:

> "The large ter-, quadri-, and pentavalent elements are extremely hydrolytic and form hydroxides, phosphates, silicates, carbides, etc., that are very insoluble and difficult to dissolve in common acids, particularly if they have been heated strongly and converted to refractory forms. For example, eight samples of soil taken in the vicinity of a plutonium-handling facility were analyzed in the facility's own laboratory for ^{239}Pu by their routine procedure involving leaching with nitric acid in the presence of ^{236}Pu tracer. The insoluble residues were then analyzed for the same radionuclide by one of the present authors using a procedure involving complete dissolution in a potassium fluoride fusion in the presence of ^{236}Pu tracer. Four of the residues contained more ^{239}Pu than the corresponding leachates, three residues contained about half as much as the leachates, and only one contained as little as 22%, largely because that sample contained relatively high activity of the radionuclide (Sill, 1981). None of the water-soluble ^{236}Pu tracer used in the original leach determination was present in any of the residues, showing that heterogeneous exchange did not occur (Sill, 1975). The original results from leaching were, therefore, grossly inaccurate."

However, there are also disadvantages and challenges associated with the fusion approach. Fusions are frequently more labor intensive than the leaching approach. More often than not, it is one sample at a time using a burner. Large quantities of the flux are generally required to decompose most substances, often 5 to10 times the sample weight. Therefore, contamination of the sample by impurities in the reagent is quite possible. Furthermore, the aqueous solutions resulting from the fusions will have a very high salt content, which may lead to difficulties in subsequent steps of the analysis, i.e., difficulties of entrainment, partial replacements, etc. The high temperatures associated with these fusions increase the danger of loss of certain analytes by volatilization. Finally, the crucible itself is often attacked by the flux, once again leading to possible contamination of the sample. The typical sample size for fusions ranges from typically one to ten grams. The analyst must consider whether a this sample is representative.

13.7.3 Acid Digestion — Fusion Combined Approach

Clearly, the sample history, as well as the analytical protocol specifications of a study, should play a significant role in the choice of analytical method. The analyst must be certain that the chosen dissolution technique will provide adequate data for the problem at hand, whether it be through acid leaching or total dissolution. However, as a compromise, it is common practice to employ a combination of the two approaches when the majority of the material to be analyzed is acid-soluble. First, an acid leach is applied to the bulk of the sample. Then any undecomposed residue is isolated by filtration and fused with a relatively small quantity of suitable flux. Finally, the melt is dissolved and combined with the rest of the sample.

Through this approach, the total matrix is decomposed, but the problems, such as reagent quantity, and sample and fusion vessel size (commonly associated with fusions), are limited. The quantities of added salt are less; therefore, the sources of contamination or of subsequent chemical interferences are reduced. Moreover, losses because of volatility tend to be less because only a small fraction of the sample is exposed to the high temperatures associated with the fusion process.

13.8 Examples of Decomposition Procedures

DECOMPOSITION OF ORGANIC MATERIAL WITH SULFURIC AND NITRIC ACIDS. Add H_2SO_4 to the sample and heat to fumes in a Kjeldahl flask. Add concentrated HNO_3 by drops to the flask, allowing the reaction to subside after each addition. Periodically heat to fuming to remove water and to keep the temperature high. When the solution is clear and colorless, the reaction is complete. Very reactive material can be left overnight in a 1:1 solution of the acids. Red or white fuming nitric acid can be used to speed up the reaction, if necessary.

DECOMPOSITION OF ORGANIC MATERIAL WITH PERCHLORIC AND NITRIC ACIDS. The acids can be added to the sample as a mixture or the sample can be treated with concentrated HNO_3 first to destroy any highly reactive material. The solution is heated to drive off the HNO_3 and to raise the temperature to 160 °C, where the $HClO_4$ begins to oxidize the organic material. The reaction is generally accompanied by foaming, and HNO_3 is used to cool the solution and to control the formation of foam. The solution should be cooled immediately if any layer of material begins to separate and turn brown. HNO_3 is added to the sample before it is returned to the hot plate. The transition into $HClO_4$ continues until the foaming is completed and dense white fumes are evolved, indicating that $HClO_4$ is being evaporated. The volume is reduced and the solution converted to HNO_3 by repeated addition of HNO_3 and evaporation to near dryness.

DECOMPOSITION OF A SAMPLE OF UNKNOWN COMPOSITION (Noyes and Bray, 1927/1943; Bock, 1979, Appendix 1). First, destroy the organic material with perchloric and nitric acids and then perform an oxidizing dissolution with HBr and Br_2. Separate the residue and oxidize it with nitric acid. Subsequently, heat to fumes with perchloric acid and HF to destroy any silicates present. Combine with the HBr solution and distill off the bromides of arsenic, germanium, and selenium. Oxidize the residue with nitric acid, add sodium peroxide, and distill off osmium as the tetroxide. Add perchloric acid and distill off ruthenium as the tetroxide. Reduce the contents of the flask with formic acid. Separate the residue, and leach with HF to dissolve niobium, tantalum, and tungsten. Separate the residue, and fuse with sodium carbonate to convert fluorides to carbonates; then dissolve the melt in dilute perchloric acid. Separate the residue, and treat with aqua regia to dissolve the gold group metals. Separate the residue, and treat with ammonia to dissolve silver. Separate the residue, and fuse with $K_2S_2O_7$; then dissolve the melt in water. Separate the residue, and fuse with sodium peroxide.

DECOMPOSITION OF SOIL FOR ACTINIDE ANALYSIS (Sill et al., 1974; Sill and Sill, 1995). Sill has described a potassium fluoride-potassium pyrosulfate fusion technique that can be used before elemental separation for the alpha-emitting nuclides of radium through californium. The organic matter of the soil is initially destroyed by heating the sample with nitric acid in a platinum crucible. To a 1 g sample, potassium fluoride is added and mixed well. The potassium fluoride fusion is carried out using a blast burner at approximately 900 °C. After the melt is cooled, concentrated sulfuric acid is added, and the mixture is heated to decompose the potassium fluoride cake, with the simultaneous volatilization of hydrogen fluoride and silicon tetrafluoride. After the cake is completely transformed, anhydrous sodium sulfate is added and the pyrosulfate fusion is performed. The resultant cake is then dissolved in dilute HCl before subsequent elemental separation.

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14 SEPARATION TECHNIQUES

14.1 Introduction

The methods for separation, collection, and detection of radionuclides are similar to ordinary analytical procedures and employ many of the chemical and physical principles that apply to their nonradioactive isotopes. However, some important aspects of the behavior of radionuclides are significantly different, resulting in challenges to the radiochemist to find a means for isolation of a pure sample for analysis (Friedlander et al., 1981, pp. 292-293).

The contents of Chapter 14 provide in one reference document: (1) a review of the important chemical principles that constitute the foundation of radiochemical separations, (2) a survey of the important separation methods used in radiochemistry with a discussion of the advantages and disadvantages of each method, and (3) an examination of the particular features of radioanalytical chemistry that differentiate it from ordinary analytical chemistry. Extensive examples have been employed throughout the chapter to illustrate various principles, practices, and procedures in radiochemistry. Many were purposely selected from agency procedural manuals to provide illustrations from familiar and available documents. Others were taken from the classical and recent radiochemical literature to afford a broad, general overview of the subject.

The material in this chapter is presented in three topic areas. It begins with a review of oxidation-reduction processes and complex-ion formation, two subjects that constitute the principal foundation of radiochemistry procedures and provide background for the topics to follow. The chapter continues with a description of separation techniques commonly found in radiochemical procedures: solvent extraction, volatilization and distillation, electrodeposition, chromatography, and precipitation and coprecipitation. It concludes with two subjects unique to radioanalytical chemistry: carriers and tracers, and radiochemical equilibrium. This organization is designed to provide a developmental approach to the description of each topic area. Explanation of the separation techniques, for example, is dependent on basic chemical principles generally known to the reader, as well as the specific principles developed in the preceding sections. Descriptions of carriers and tracers, and radiochemical equilibrium are contingent on an adequate knowledge of preceding topics, and their explanation makes extensive use of the principles developed in these sections. In all sections of Chapter 14, specific radionuclide examples are used to illustrate the principles and practices involved. Practical guidance is also provided for the practicing radiochemist.

Because the radiochemist detects atoms by their radiation, the success or failure of a radiochemical procedure often depends on the ability to separate extremely small quantities of radionuclides (e.g., 10^{-6} to 10^{-12} g) that might interfere with detection of the analyte. For example,

isolation of trace quantities of a radionuclide that will not precipitate on their own with a counter-ion requires judicious selection of a carrier and careful technique to produce a coprecipitate containing the pure radionuclide, free of interfering ions. In detection procedures, the differences in the behavior of radionuclides provide unique opportunities not available in the traditional analytical chemistry of nonradioactive elements. Radionuclides can often be detected by their unique radiation regardless of the chemical form of the element. There is also a time factor involved, because of the short half-lives of some radionuclides. Traditional procedures involving long digestions or slow filtrations cannot be used for short-lived radionuclides, thereby requiring that rapid separations be developed. Another distinction is the hazards associated with radioactive materials. At very high activity levels (radiolysis), chemical effects of the radiation, such as decomposition of solvents and heat effects, can affect the procedures. Equally important, even at lower activity levels, is the radiation dose (especially with gamma-emitters) that the radiochemist can receive unless protected by shielding or distance. Even at levels where the health concerns are minimal, special care needs to be taken to guard against laboratory and equipment contamination. Moreover, the modern radiochemist should be concerned about the type and quantity of the waste generated by the chemical procedures employed, because the costs and difficulties associated with the disposal of low-level and mixed radioactive waste continue to rise. A review of the basic chemical principles that apply to the analysis of radionuclides is presented in this chapter with an emphasis on the unique behavior of radionuclides.

14.2 Oxidation/Reduction Processes

14.2.1 Introduction

Oxidation and reduction (redox) processes play an important role in radioanalytical chemistry, particularly from the standpoint of the dissolution, separation, and detection of analytes, tracers, and carriers. Ion exchange, solvent extraction, and solid-phase extraction separation techniques, for example, are highly dependent upon the oxidation state of the analytes. Moreover, most radiochemical procedures involve the addition of a carrier or isotope tracer, and to achieve quantitative yields, there should be complete equilibration (isotopic exchange) between the added isotope(s) and all the analyte species present. The oxidation number of a radionuclide can affect its (1) chemical stability in the presence of water, oxygen, and other natural substances in solution; (2) reactivity with reagents used in the radioanalytical procedure; (3) solubility in the presence of other ions and molecules; and (4) behavior in the presence of carriers and tracers. The oxidation numbers of radionuclides in solution and their susceptibility to change, because of natural or induced redox processes, are critical, therefore, to the physical and chemical behavior of radionuclides during these analytical procedures. The differences in mass number of all

radionuclides of an element are so small that elements with the same oxidation number will exhibit the same chemical behavior during radiochemical analysis.

14.2.2 Oxidation-Reduction Reactions

An *oxidation-reduction reaction* (*redox reaction*) is a reaction in which electrons are redistributed among the atoms, molecules, or ions in the reaction. In some redox reactions, electrons are actually transferred from one reacting species to another. *Oxidation* under these conditions is defined as the loss of electron(s) by an atom or other chemical species, whereas *reduction* is the gain of electron(s). Two examples will illustrate this type of redox reaction:

$$U + 3\,F_2 \rightarrow U^{+6} + 6\,F^{-1}$$

$$Pu^{+4} + Fe^{+2} \rightarrow Pu^{+3} + Fe^{+3}$$

In the first reaction, uranium (U) loses electrons, becoming a cation, and fluorine (F) gains an electron, becoming an anion. In the second reaction, the reactants are already ions, but the plutonium cation (Pu^{+4}) gains electrons, becoming Pu^{+3}, and the ferrous ion (Fe^{+2}) loses electrons, becoming Fe^{+3}.

In other redox reactions, electrons are not completely transferred from one reacting species to another: the *electron density* about an atom decreases, while it increases about another atom. The change in electron density occurs as covalent bonds, in which electrons are shared between two atoms, are broken, and/or are made during a chemical reaction. In covalent bonds between two atoms of different elements, one atom is more *electronegative* than the other atom. Electronegativity is the ability of an atom to attract electrons in a covalent bond. One atom, therefore, attracts the shared pair of electrons more effectively, causing a difference in electron density about the atoms in the bond. An atom that ends up bonded to a more electronegative atom at the end of a chemical reaction loses net electron density. Conversely, an atom that ends up bonded to a less electronegative atom gains net electron density. Electrons are not transferred completely to other atoms, and ions are not formed because the electrons are still shared between the atoms in the covalent bond. *Oxidation,* in this case, is defined as the loss of electron density, and *reduction* is defined as the gain of electron density. When carbon (C) is oxidized to carbon dioxide (CO_2) by oxygen (O_2):

$$C + O_2 \rightarrow CO_2$$

the electron density associated with the carbon atom decreases, and that of the oxygen atoms increases, because the electronegativity of oxygen is greater than the electronegativity of carbon. In this example, carbon is oxidized and oxygen is reduced. Another example from the chemistry of the preparation of gaseous uranium hexafluoride (UF_6) illustrates this type of redox reaction:

$$3UF_4 + 2ClF_3 \rightarrow 3UF_6 + Cl_2$$

Because the order of electronegativity of the atoms increases in the order U<H<F, the uranium atom in uranium tetrafluoride (UF_4) is oxidized further as more electronegative fluorine atoms are added to the metal and shift the electron density away from uranium. Chlorine atoms break their bonds with fluorine and gain electron density (are reduced) as they bond with each other instead of the more electronegative fluorine atoms.

In a redox reaction, at least one species is oxidized, and at least one species is reduced simultaneously; one process cannot occur without the other. The *oxidizing agent* is defined as the substance that causes oxidation of another species by accepting electron(s) from it or increasing in electron density; it is thereby reduced itself. *Reducing agents* lose electron(s) or electron density and are therefore oxidized. In the reduction of Pu^{+4} to Pu^{+3} by the ferrous ion, Fe^{+2}, the reducing agent donates an electron to Pu^{+4} and is itself oxidized, while Pu^{+4}, the oxidizing agent, accepts an electron from Fe^{+2} and is reduced. Generally, the nonmetallic elements are strong oxidizing reagents, and the metals are strong reducing agents.

To keep track of electrons in oxidation-reduction reactions, it is useful to assign oxidation numbers to atoms undergoing the changes. *Oxidation numbers* (*oxidation states*) are a relative indication of the electron density associated with an atom of an element. The numbers change during redox reactions, whether they occur by actual transfer of an electron(s) or by unequal sharing of electrons in a covalent bond. The number increases as the electron density decreases; it decreases as the electron density increases. From the standpoint of oxidation numbers and in more general terms, oxidation is defined as an increase in oxidation number, and reduction is defined as the decrease in oxidation number. Different sets of rules have been developed to assign oxidation numbers to monatomic ions and to each individual atom in molecules and ions. One set of rules is simple and especially easy to use. It can be used to determine the oxidation number of atoms in many, but not all, chemical species. In this set, the rules for assigning oxidation numbers are listed in order by priority of application; that is, the rule written first in the list has priority over the rule below it. The rules are applied in the order in which they come in the list, starting at the top and proceeding down the list of rules until each atom of each element, not the element only, in a species has been assigned an oxidation number. Generally, all atoms of each element in a chemical species will have the same oxidation number in that species. (A

specific exception would be nitrogen in the cation and anion in ammonium nitrate, NH_4NO_3.) It is important to remember that in many cases, oxidation numbers are not actual electrical charges, but only a helpful bookkeeping method for following redox reactions or examining various oxidation states. As we will see below, the oxidation number of atoms in isolated elements and monatomic ions are actually the charge on the chemical species. The priority rules are:

1. The sum of oxidation numbers of all atoms in a chemical species adds up to equal the charge on the species. This is zero for elements and compounds because they are electrically neutral species and are the total charge for a monatomic or polyatomic ion.

2. The alkali metals (the IA elements, Li, Na, K, Rb, Cs, and Fr) have an oxidation number of +1; the alkaline earth metals (the IIA elements, Be, Mg, Ca, Sr, Ba, and Ra) have an oxidation number of +2.

3. Fluorine (F) has an oxidation number of -1; hydrogen (H) has an oxidation number of +1.

4. Oxygen has an oxidation number of -2.

5. The halogens (the VIIA elements, F, Cl, Br, I, and At) have an oxidation number of -1.

6. In binary compounds (compounds containing elements), the oxidation number of the oxygen family of elements (the VIA elements, O, S, Se, Te, and Po) is -2; for the nitrogen family of elements (the VA elements except Bi, N, P, As, and Sb), it is -3.

Applying these rules illustrates their use:

1. The oxidation number of metallic uranium and molecular oxygen is 0. Applying rule one, the charge on elements is 0.

2. The oxidation number of Pu^{+4} is +4. Applying rule one again, the charge is +4.

3. The oxidation numbers of carbon and oxygen in CO_2 are +4 and -2, respectively. Applying rule one, the oxidation numbers of each atom must add up to the charge of 0 because carbon dioxide is a molecule. The next rule that applies is rule four. Therefore, the oxidation number of each oxygen atom is -2. The oxidation number of carbon is determined by C + 2(-2) = 0, or +4. Notice that there is no charge on carbon and oxygen in carbon dioxide because the compound is molecular and does not consist of ions.

4. The oxidation numbers of calcium and hydrogen in calcium hydride (CaH_2) are +2 and -1, respectively. The compound is neutral, and the application of rule one requires that the oxidation numbers of all atoms add up to 0. By rule two, the oxidation number of calcium is +2. Applying rule one, the oxidation number of hydrogen is: 2H + 2=0, or -1. Notice that in this example, the oxidation number as predicted by the rules does not agree with rule three, but the number is determined by rules one and two, which take precedence over rule three.

5. The oxidation numbers of uranium and oxygen in the uranyl ion, UO_2^{+2}, are +6 and -2, respectively. Applying rule one, the oxidation numbers of each atom must add up to the charge of +2. Rule four indicates that the oxygen atoms are -2 each. Applying rule one, the oxidation number of uranium is U + 2(-2) = +2, and uranium is +6. In this example, the charges on uranium and oxygen are not actually +6 and -2, respectively, because the polyatomic ion is held together through covalent bonds. The charge on the ion is the result of a deficiency of two electrons.

Oxidation numbers (states) are commonly represented by zero and positive and negative numbers, such as +4, -2, etc. They are sometimes represented by Roman numerals for metals, especially the oxidation numbers of atoms participating in covalent bonds of a molecule or those of polyatomic ions. Uranium in UO_2^{+2} can be represented as U(VI) instead of U^{+6}, or chromium in CrO_4^{-2} as Cr(VI) rather than Cr^{+6}.

14.2.3 Common Oxidation States

Some radionuclides, such as cesium (Cs) and thorium (Th), exist in solution in single oxidation states, as indicated by their position in the periodic table. Others, such as technetium (Tc) and uranium (U), can exist in multiple oxidation states. Multiple oxidation states of plutonium (Pu) are commonly found in the same solution.

The oxidation state for any element in its free state (when not combined with any other element, as in Cl_2 or Ag metal) is zero. The oxidation state of a monatomic ion is equal to the electrical charge of that ion. The Group IA elements form ions with a single positive charge (Li^{+1}, Na^{+1}, K^{+1}, Rb^{+1}, and Cs^{+1}), whereas the Group IIA elements form +2 ions (Be^{+2}, Mg^{+2}, Sr^{+2}, Ba^{+2}, and Ra^{+2}). The halogens generally form -1 ions (F^{-1}, Br^{-1}, Cl^{-1}, and I^{-1}); however, except for fluorine, the other halogens form oxygen compounds in which several other oxidation states are present [Cl(I) in HClO and I(V) in HIO_3]. For example, iodine can exist as I^{-1}, I_2, IO^{-1}, IO_3^{-1}, and IO_4^{-1}. Oxygen exhibits a -2 oxidation state except when its bonded to fluorine, where it can be +1 or +2; in peroxides, where the oxidation state is -1; and in superoxides, where it is -½.

Each of the transition metals has at least two stable oxidation states, except for Sc, Y, and La (Group IIIB), which exhibit only the +3 oxidation state. Generally, negative oxidation states are not observed for these metallic elements. The large number of oxidation states exhibited by the transition elements leads to an extensive, often complicated, oxidation-reduction chemistry. For example, oxidation states from -1 through +7 have been observed for technetium, although the +7 and +4 are most common (Anders, 1960, p. 4). In an oxidizing environment, Tc exists predominantly in the heptavalent state as the pertechnetate ion, TcO_4^{-1}, which is water soluble, but which can yield insoluble salts with large cations. Technetium forms volatile heptoxides and acid-insoluble heptasulfides. Subsequently, pertechnetate is easily lost upon evaporation of acid solutions unless a reducing agent is present or the evaporation is conducted at low temperatures. Technetium(VII) can be reduced to lower oxidation states by reducing agents such as bisulfite (HSO_3^{-1}). This process proceeds through several intermediate steps, some of which are slow; therefore, unless precautions are taken to maintain technetium in the appropriate oxidation state, erratic results can be obtained. The +7 and +4 ions behave very differently in solution. For instance, pertechnetate does not coprecipitate with ferric hydroxide, while Tc(IV) does.

The oxidation states of the actinide elements have been comprehensively discussed by Ahrland (1986, pp. 1480-1481) and Cotton and Wilkinson (1988, pp. 985-987 and pp. 1000-1014). The actinides exhibit an unusually broad range of oxidation states, of from +2 to +7 in solution. Similar to the lanthanides, the most common oxidation state is +3 for actinium (Ac), americium (Am), and curium (Cm). The +4 state is common for thorium and plutonium, whereas +5 is most common for protactinium (Pa) and neptunium (Np). The most stable state for uranium is the +6 oxidation state.

In compounds of the +3 and +4 oxidation states, the elements are present as simple M^{+3} or M^{+4} cations; but for higher oxidation states, the most common forms in compounds and in solution are the oxygenated actinyl ions, MO_2^{+1} and MO_2^{+2}:

- M^{+3}. The +3 oxidation state is the most stable condition for actinium, americium, and curium. It is easy to produce Pu^{+3}. This stability is of critical importance to the radiochemistry of plutonium. Many separation schemes take advantage of the fact that Pu can be selectively maintained in either the +3 or +4 oxidation state. Unlike Pu and Np, U^{+3} is such a strong reducing agent that it is difficult to keep in solution.

- M^{+4}. The only oxidation state of thorium that is experienced in radiochemical separations is +4. Pa^{+4}, U^{+4}, and Np^{+4} are stable, but they are easily oxidized by O_2. In acid solutions with low plutonium concentrations, Pu^{+4} is stable. Americium and curium can be oxidized to the +4 state with strong oxidizing agents such as persulfate.

- M^{+5}. The actinides from protactinium through americium form MO_2^{+1} ions in solution. PuO_2^{+1} can be the dominant species in solution at low concentration in natural waters that are relatively free of organic material.

- M^{+6}. M+6 is the most stable oxidation state of uranium, which exist as the UO_2^{+2} species. Neptunium, plutonium, and americium also form MO_2^{+2} ions in solution. The bond strength, as well as the chemical stability toward reduction for these MO_2^{+2} ions, decrease in the order U > Np > Pu > Am.

Reactions that do not involve making or breaking bonds, $M^{+3} \rightarrow M^{+4}$ or $MO_2^{+1} \rightarrow MO_2^{+2}$, are fast and reversible, while reactions that involve chemical bond formation, $M^{+3} \rightarrow MO_2^{+1}$ or $M^{+4} \rightarrow MO_2^{+2}$, are slow and irreversible.

Plutonium exhibits redox behavior unmatched in the periodic table. It is possible to prepare solutions of plutonium ions with appreciable concentrations of four oxidation states, +3, +4, +5, and +6, as Pu^{+3}, Pu^{+4}, PuO_2^{+1}, and PuO_2^{+2}, respectively. [Detailed discussions can be found in Cleveland (1970), Seaborg and Loveland (1990), and in the Coleman (1965) monograph.] According to Cleveland (1970), this polyvalent behavior occurs because of the tendency of Pu^{+4} and Pu^{+5} to disproportionate:

$$3Pu^{+4} + 2H_2O \rightarrow 2Pu^{+3} + PuO_2^{+2} + 4H^{+1}$$

$$3PuO_2^{+1} + 4H^{+1} \rightarrow Pu^{+3} + 2PuO_2^{+2} + 2H_2O$$

and because of the slow rates of reaction involving formation or rupture of Pu-O bonds (such as PuO_2^{+} and PuO_2^{2+}) compared to the much faster reactions involving only electron transfer. The distribution depends on the type and concentration of acid used for dissolution, the method of solution preparation, and the initial concentration of the different oxidation states. In HCl, HNO_3, and $HClO_4$, appreciable concentrations of all four states exist in equilibrium. Seaborg and Loveland (1990, p. 88) report that in 0.5 M HCl at 25 °C, the equilibrium percentages of plutonium in the various oxidation states are found to be as follows:

Pu^{+3}	27.2%
Pu^{+4}	58.4%
Pu^{+5}	~0.7%
Pu^{+6}	13.6%

Apart from the disproportionation reactions, the oxidation state of plutonium ions in solution is affected by its own decay radiation or external gamma and X-rays. Radiolysis products of the solution can oxidize or reduce the plutonium, depending on the nature of the solution and the oxidation state of plutonium. Therefore, the stated oxidation states of old plutonium solutions, particularly old $HClO_4$ and H_2SO_4 solutions, should be viewed with suspicion. Plutonium also tends to hydrolyze and polymerize in solution, further complicating the situation (see Section 14.10, *Radiochemical Equilibrium*).

Tables 14.1 and 14.2 summarize the common oxidation number(s) of some important elements encountered in the radioanalytical chemistry of environmental samples and the common chemical form of the oxidation state.

TABLE 14.1 — Oxidation states of elements[1]

Element	Oxidation State[2]	Chemical Form	Notes
Am	+3	Am^{+3}	Pink; stable; difficult to oxidize
	+4	Am^{+4}	Pink-red; unstable in acid
	+5	AmO_2^{+1}	Pink-yellow; disproportionates in strong acid; reduced by products of its own radiation
	+6	AmO_2^{+2}	Rum color; stable
Cs	+1	$Cs(H_2O)_x^{+1}$	Colorless; x probably is 6
Co	+2	$Co(H_2O)_6^{+2}$	Pink to red; oxidation is very unfavorable in solution
	+3	$Co(H_2O)_6^{+3}$	Rapidly reduced to +2 by water unless acidic
Fe	+2	$Fe(H_2O)_6^{+2}$	Green
	+3	$Fe(H_2O)_6^{+3}$	Pale violet; hydrolyses in solution to form yellow or brown complexes
^3H	+1	^3HOH and $^3HOH_2O^{+1}$	Exchange of tritium is extremely rapid in samples that have water introduced.
I	-1	I^{-1}	Colorless
	-1/3	I_3^{-1}	Brown; commonly in solutions of I^{-1} exposed to air
	+5	IO_3^{-1}	Colorless; formed in vigorously oxidized solutions
	+7	IO_4^{-1}	Colorless
Ni	+2	$Ni(H_2O)_6^{+2}$	Green
Nb	+3	Unknown	In sulfuric acid solutions of Nb_2O_5
	+5	$HNb_6O_{19}^{-7}$	
Po	+4		

Element	Oxidation State[2]	Chemical Form	Notes
Pu	+3	$Pu(H_2O)_x^{+3}$	Violet; stable to air and water; easily oxidized to +4
	+4	$Pu(H_2O)_x^{+4}$	Tan; first state formed in freshly prepared solutions; stable in 6 M acid; disproportionates in low acidity to +3 and +6
	+5	$Pu(H_2O)_x^{+5}$	Never observed alone; always disproportionates; most stable in low acidity
		or	
		PuO_2^{+5}	Purple
	+6	PuO_2^{+5}	Yellow-pink; stable but fairly easy to reduce
	+7	PuO_5^{-3}	Green
		or	
		$PuO_4(OH)_2^{-3}$	$PuO_4(OH)_2^{-3}$ more likely form
Ra	+2	$Ra(H_2O)_x^{+2}$	Colorless; behaves chemically like Sr and Ba
Sr	+2	$Sr(H_2O)_x^{+2}$	Colorless
Tc	+4	TcO_3^{-2}	
	+5	TcO_3^{-1}	
	+7	TcO_4^{-1}	
Th	+4	$Th(H_2O)_8^{+4}$	Colorless; at pH>3 forms complex hydrolysis products
U	+3	$U(H_2O)_x^{+3}$	Red-brown; slowly oxidized by water and rapidly by air to +4
	+4	$U(H_2O)_{8-9}^{+4}$	Green; stable but slowly oxidized by air to +6
	+5	UO_2^{+1}	Unstable but more stable at ph 2-4; disproportionates to +4 and +6
	+6	$UO_2(H_2O)_5^{+}$	Yellow; only form stable in solution containing air; difficult to reduce
Zr	+4	$Zr(H_2O)_6^{+4}$	Only at very low ion concentrations and high acidity
		$Zr_4(OH)_8(H_2O)_{16}^{+2}$	At typical concentrations in absence of complexing agents

(1) Compiled from: Booman and Rein, 1962; Cotton and Wilkinson, 1988; Emsley, 1989; Greenwood and Earnshaw, 1984; Grinder, 1962; Hampel, 1968; Katzin, 1986; Latimer, 1952; and Pauling, 1970.
(2) Most common form is in bold.

TABLE 14.2 — Stable oxidation states of selected elements [1,2]

Element	+1	+2	+3	+4	+5	+6	+7	+8
Titanium		○	○	●				
Vanadium		○	○	●	●			
Chromium		●	●	○	○	●		
Manganese		●	○	●	○	○	●	
Iron		●	●	○		○		
Cobalt		●	●					
Nickel		●	○	○				
Strontium		●						
Yttrium			●					
Molybdenum		○	○	●	●	●		

Element	+1	+2	+3	+4	+5	+6	+7	+8
Technetium		○	○	●	○	○	●	
Silver	●		○	○				
Cesium	●							
Barium		●						
Lanthanides			●					
Lead		●		○				
Polonium		○		●		○		
Radium		●						
Actinium			●					
Thorium				●				
Protactinium				○	●			
Uranium			○	○	○	●		
Neptunium			○	○	●	○	○	
Plutonium			○	●	○	○		
Americium			●	○	○	○		
Curium			●	○				

(1) The stable nonzero oxidation states are indicated. The more common oxidation states are indicated by solid black circles.
(2) Data compiled from Seaborg and Loveland (1990) and the NAS–NRC monographs listed in the references.

14.2.4 Oxidation State in Solution

For the short-lived isotopes that decay by alpha emission or spontaneous fission, high levels of radioactivity cause heating and chemical effects that can alter the nature and behavior of the ions in solution and produce chemical reactions not observed with longer-lived isotopes. Decomposition of water by radiation (*radiolysis*) leads to H and OH free radicals and formation of H_2 and H_2O_2, among other reactive species, and higher oxidation states of plutonium and americium are produced.

The solutions of some ions are also complicated by *disproportionation*, the autooxidation-reduction of a chemical species in a single oxidation state to higher and lower oxidation states. The processes are particularly dependent on the pH of the solution. Oxidation of iodine, uranium, americium, and plutonium are all susceptible to this change in solution. The disproportionation of UO_2^{+1}, for example, is represented by the chemical equation:

$$2\ UO_2^{+1} + 4\ H^{+1} \rightarrow U^{+4} + UO_2^{+2} + 2\ H_2O \quad (K = 1.7 \times 10^6)$$

The magnitude of the equilibrium constant reflects the instability of the +5 oxidation state of uranium in UO_2^{+1} described in Table 14.1, and the presence of hydrogen ions reveals the influence of acidity on the redox process. An increase in acidity promotes the reaction.

14.2.5 Common Oxidizing and Reducing Agents

HYDROGEN PEROXIDE. Hydrogen peroxide (H_2O_2) has many practical applications in the laboratory. It is a very strong oxidizing agent that will spontaneously oxidize many organic substances, and water samples are frequently boiled with peroxide to destroy organic compounds before separation procedures. When hydrogen peroxide serves as an oxidizing reagent, each oxygen atom changes its oxidation state from -1 to -2. For example, the reaction for the oxidation of ferrous ion is as follows:

$$H_2O_2 + 2H^{+1} + 2Fe^{+2} \rightarrow 2H_2O + 2Fe^{+3}$$

Hydrogen peroxide is frequently employed to oxidize Tc^{+4} to the pertechnetate:

$$4H_2O_2 + Tc^{+4} \rightarrow TcO_4^{-1} + 4H_2O$$

Hydrogen peroxide can also serve as a reducing agent, with an increase in oxidation state from -1 to 0, and the liberation of molecular oxygen. For example, hydrogen peroxide will reduce permanganate ion (MnO_4^{-1}) in basic solution, forming a precipitate of manganese dioxide:

$$2MnO_4^{-1} + 3H_2O_2 \rightarrow 2MnO_2\downarrow + 3O_2\uparrow + 2H_2O + 2\,OH^{-1}$$

Furthermore, hydrogen peroxide can decompose by the reaction:

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

This reaction is another example of a disproportionation (autooxidation-reduction) in which a chemical species acts simultaneously as an oxidizing and reducing agent; half of the oxygen atoms are reduced to O^{-2}, and the other half are oxidized to elemental oxygen (O^0) in the diatomic state, O_2.

OXYANIONS. Oxyanions (NO_3^{-1}, $Cr_2O_7^{-2}$, ClO_3^{-1}, and MnO_4^{-1}) differ greatly in their oxidizing strength, but they do share certain characteristics. They are stronger oxidizing agents in acidic rather than basic or neutral conditions, and they can be reduced to a variety of species depending

on the experimental conditions. For example, on reduction in acidic solutions, the permanganate ion accepts five electrons, forming the manganous ion Mn^{+2}:

$$MnO_4^{-1} + 5e^{-1} + 8H^{+1} \rightarrow Mn^{+2} + 4H_2O$$

In neutral or basic solution, permanganate accepts 3 electrons, and forms manganese dioxide (MnO_2), which precipitates:

$$MnO_4^{-1} + 3e^{-1} + 4H^{+1} \rightarrow MnO_2 \downarrow + 2H_2O$$

These oxidizing agents are discussed further in Section 12.4, "Wet Ashing and Acid Dissolution Techniques."

NITRITE. Nitrite ion (NO_2^{-1}), plays an important role in the manipulation of Pu oxidation states in solution. It is capable of oxidizing Pu^{+3} to Pu^{+4} and of reducing Pu^{+6} to Pu^{+4}. Because most aqueous processes center around Pu^{+4}, sodium nitrite ($NaNO_2$) is frequently used as a valence adjuster to convert all Pu to the +4 state. And because the $Pu^{+6} \rightarrow Pu^{+4}$ reaction by nitrite is slow, another reducing agent, such as the ferrous ion, often is added to increase the rate of reaction.

PERCHLORIC ACID. The use of perchloric acid ($HClO_4$) as an oxidizing agent is covered in depth in Section 12.4, "Wet Ashing and Acid Dissolution Techniques."

METALS IONS. Generally, metals ions (Ti^{+3}, Cr^{+2}, Fe^{+2}, etc.) are strong reducing agents. For example, both Ti^{+3} and Cr^{+2} have been shown to reduce Pu^{+4} to Pu^{+3} rapidly in acidic media. Fe^{+2} rapidly reduces Np^{+5} to Np^{+4} in H_2SO_4.

Ti^{+3} is used extensively as a reducing agent in both inorganic and organic analyses. Ti^{+3} is obtained by reducing Ti^{+4}, either electrolytically or with zinc. Ti^{+4} is the most stable and common oxidation state of titanium. Compounds in the lower oxidation states (-1, 0, +2, and +3) are quite readily oxidized to Ti^{+4} by air, water, or other reagents.

ASCORBIC ACID. Commonly known as vitamin C, ascorbic acid is an important reducing agent for the radiochemist. Because the ferric ion interferes with the uptake of Am^{+3} in several popular extraction schemes, ascorbic acid is frequently used to reduce Fe^{+3} to Fe^{+2} to remove this interference. Ascorbic acid is also used to reduce Pu^{+4} to Pu^{+3}.

14.2.6 Oxidation State and Radiochemical Analysis

Most radiochemical analyses require the radionuclide be in aqueous solution. Thus, except for water samples, the first step of an analysis is the complete dissolution of the sample so that all components remaining at the end of the process are in a true solution. Dissolution of many samples requires vigorous conditions to release the radionuclides from its natural matrix. Strong mineral acids or strong bases, which also serve as powerful oxidizing agents, are used in boiling mixtures or under fusion conditions to decompose the matrix—evaporating portions of the acid or base from the mixture and oxidizing the radionuclide to a common oxidation state. The final state depends, generally, on the radionuclide, oxidizers used, and pH of the solution (see notes in Table 14.1, Section 14.2.3, "Common Oxidation States"). Even water samples might contain radionuclides at various states of oxidation because of their exposure to a variety of natural oxidizing conditions in the environment and the pH of the sample.

Once the analyte is in solution, the radioelement and the tracers and carriers used in the procedure must be in the same oxidation state to ensure the same chemical behavior (Section 14.10.2, "Oxidation State"). For radionuclides that can exist in multiple oxidation states, one state must be achieved; for those such as plutonium, which disproportionates, a reproducible equilibrium mixture of all oxidation states can be established. Oxidizing or reducing agents are added to the reaction mixture to establish the required conditions. Table 14.3 contains a summary of several chemical methods for the oxidation and reduction of select radionuclides.

TABLE 14.3 — Redox reagents for radionuclides[1]

Redox Reaction	Reagent	Conditions
$Am^{+3} - AmO_2^{+2}$	Ag^{+2}, Ag^{+}/S_2O_8	
$Am^{+4} - AmO_2^{+2}$	O_3	13 M NH_4F
$AmO_2^{+1} - AmO_2^{+2}$	Ce^{+4}	$HClO_4$
	O_3	Heated HNO_3 or $HClO_4$
$AmO_2^{+2} - AmO_2^{+1}$	Br^{-1}, Cl^{-1}	
	Na_2CO_3	Heat to precipitate $NaAmO_2CO_3$; dissolve in H^{+1}
$AmO_2^{+2} - Am^{+3}$	I^{-1}, H_2O_2, NO_2^{-1}, SO_2	
$Am^{+4} - Am^{+3}$	alpha radiation effects	Spontaneous
$Co^{+2} - Co^{+3}$	O_3	Cold $HClO_4$
	O_2, H_2O_2	Complexed cobalt
$Co^{+3} - Co^{+2}$	H_2O	Rapid with evolution of H_2
$Fe^{+2} - Fe^{+3}$	O_2	Faster in base; slower in neutral and acid solution; decreases with H^{+1}
	Ce^{+4}, MnO_4^{-1}, NO_3^{-1}, NO_2^{-}	
	H_2O_2, $S_2O_8^{-2}$	

	Redox Reaction	Reagent	Conditions
		$Cr_2O_7^{-2}$	HCl or H_2SO_4
413	$Fe^{+3} - Fe^{+2}$	H_2S, H_2SO_3	Excess removed by boiling
		Zn, Cd, Al, Ag amalgams	
		Sn^{+2}, I^{-1}, Cu^{+1}, Ti^{+3}	
		NH_2OH	Boiling solution
414	$I^{-1} - I_2$	HNO_2 ($NaNO_2$ in acid)	Does not affect other halides
		MnO_2 in acid	Well suited for lab work
		6M HNO_3	
		$NaHSO_3$ or $NaHSO_3$ in H^{+1}	
		Na_2SO_3; $Na_2S_2O_3$	
415	$I^{-1} - IO_3^{-1}$	$KMnO_4$	
		50% CrO_3 in 9M H_2SO_4	
416	$I^{-1} - IO_4^{-1}$	NaClO in base	
417	$IO_4^{-1} - I_2$	$NH_2OH \cdot HCl$	
		$H_2C_2O_4$	(9 M H_2SO_4
418	$IO_4^{-1} - I^{-1}$	$NaHSO_3$ in acid	
419	$I_2 - I^{-1}$	SO_2; $NaHSO_3$	
420	$Pu^{+3} - Pu^{+4}$	BrO_3^{-1}	Dilute H^{+1}
		Ce^{+4}	HCl of H_2SO_4 solution
		$Cr_2O_7^{-2}$, IO_3^{-1}, MnO_4^{-1}	Dilute H^{+1}
		NO_2^{-1}	HNO_3
		NO_3^{-1}	HNO_3 or dilute HCl (100°C)
		HNO_2	
421	$Pu^{+4} - PuO_2^{+2}$	$NaBiO_3$	HNO_3
		BrO_3^{-1}	Dilute HNO_3 at 85°C
		Ce^{+4}	Dilute HNO_3 or $HCLO_4$
		HOCl (KClO)	pH 4.5 at 80°C or 45% K_2CO_3 at 40°C
		MnO_4^{-1}	Dilute HNO_3
		O_3	Ce^{+4} or Ag^{+1} catalyst or dil. H_2SO_4/60°C
		Ag(II)	$Ag^{+1}/S_2O_8^{-1}$ in dil. HNO_3
		$Cr_2O_7^{-2}$	Dilute H_2SO_4
		Cl_2	Dilute H_2SO_4 at 80°C or dil.$HClO_4/Cl^{-1}$
		NO_3^{-1}	Dilute HNO_3 at 95°C
		Ag_2O	43% K_2CO_3 at 75°C
		IO_3^-	
422	$PuO_2^{+1} - PuO_2^{+2}$	HNO_3	Dilute; slow
		$NH_2OH \cdot HCl$	Slow
		I^{-1}	pH 2; slow
		SO_2	Dilute H^{+1}; slow
		V^{+3} or Ti^{+3}	$HClO_4$; slow
423	$PuO_2^{+2} - PuO_2^{+1}$	I^{-1}	pH 2

	Redox Reaction	Reagent	Conditions
		SO_2	H^{+1}
		Fe^{+2}	$HClO_4$ or HCl
		V^{+3} or U^{+4}	$HClO_4$
		HNO_2	dil. HNO_3NaNO_3
		Ag	dil. HCl
424	$PuO_2^{+2} - Pu^{+4}$	$C_2O_4^{-2}$	75°C; RT with dil. HCl
		I^{-1}	HNO_3
		Fe^{+2}	HCl, HNO_3, or H_2SO_4
		Sn^{+2}	$HCl/HClO_4$
		H_2O_2	HNO_3; continues to Pu^{+3} in absence of Fe^{+3}
		Ti^{+3}	$HClO_4$
		Cu_2O	45% K_2CO_3 75°C
		HNO_2	HNO_3/75°C
		Zn	dil. HCl
425	$PuO_2^{+1} - Pu^{+4}$	HNO_2	slow
		$NH_2OH{\cdot}HCl$	dil. HCl, slow
426	$Pu^{+4} - Pu^{+3}$	hydroquinone	dil. HNO_3
		H_2/Pt	HCl
		I^{-1}	dil. HCl
427		HSO_3^{-1}	dil. HNO_3
		$NH_2OH{\cdot}HCl$	
		Zn	dil. HCl
		SO_2	dil. HNO_3
		Ti^{+3}	HCl, dil. H_2SO_4, or dil. HNO_3/H_2SO_4
		ascorbic acid	HNO_3
		U^{+4}	dil. $HClO_4$
		H_2S	dil. acid
428	$Tc^{+4} - TcO_4^{-1}$	HNO_3	
		H_2O_2	
		O_2 (air)	
429	TcO_2(hydrated) –	Ce^{+4}	
430	TcO_4^{-1}		
		H_2O_2	
431	$TcCl_6^{-2} - TcO_4^{-1}$	HNO_3	
		H_2O_2	
		Cl_2	
		Ce^{+4}	
		MnO_4^{-1}	
432	$TcO_4^{-1} - Tc^{+4}$ or	N_2H_4	dil. H_2SO_4
433	TcO_2(hyd)		
		NH_2OH	dil. H_2SO_4
		ascorbic acid	dil. H_2SO_4

Redox Reaction	Reagent	Conditions
	Sn^{+2}	dil. H_2SO_4
	Zn	dil. HCl
	Conc. HCl	to $TcCl_6^{-2}$
$U^{+3} - U^{+4}$	ClO_4^{-1}	dil. $HClO_4$
	Co^{+3} complexes	dil. $HClO_4$ or $LiClO_4$
	Cr^{+3} and Cr^{+3} complexes	dil. $HClO_4$ or $LiClO_4$
	H_2O	dil. or conc. HCl or H_2SO_4
	UO_2^{+1}	dil. $HClO_4$
	UO_2^{+2}	dil. $HClO_4$
	O_2 (air)	
$U^{+4} - UO_2^{+2}$	Br_2	catalyzed by Fe^{+3} or Mn^{+2}
	BrO_3^{-1}	$HClO_4$
	Ce^{+4}	dil. $HClO_4$
	ClO_3^{-1}	catalyzed by Fe^{+2} or V^{+5}
	Fe^{+3}	
	$HClO_2$	phenol
	$HCrO_4^{-1}$	
	HNO_2	catalyzed by Fe^{+2}
	HNO_3	
	H_2O_2	
	O_2	
	Pu^{+4}	
	PuO_2^{+2}	
	MnO_2	
$UO_2^{+1} - UO_2^{+2}$	Fe^{+3}	
$UO_2^{+2} - U^{+4}$	Cr^{+2}	
	Eu^{+2}	
	Np^{+3}	
	Ti^{+3}	
	V^{+2} and V^{+3}	
$UO_2^{+2} - U^{+3}$	Zn(Hg)	
$UO_2^{+1} - U^{+4}$	Cr^{+2}	
	H_2	
	Zn(Hg)	

(1) Compiled from: Anders, 1960; Bailar et al., 1984; Bate and Leddicotte, 1961; Cobble, 1964; Coleman, 1965; Cotton and Wilkinson, 1988; Greenwood and Earnshaw, 1984; Hassinsky and Adloff, 1965; Kleinberg and Cowan, 1960; Kolthoff et al., 1969; Latimer, 1952; Metz and Waterbury, 1962; Schulz and Penneman, 1986; Weigel, 1986; and Weigel et al., 1986.

In some radioanalytical procedures, establishing different states at different steps in the procedure is necessary to ensure the requisite chemical behavior of the analyte.

One method for the analysis of ^{129}I in aqueous solutions illustrates the use of oxidation and reduction chemistry to bring the radionuclide to a specific oxidation state so that it can be isolated from other radionuclides and other elements (DOE, 1995, Method RP230). Iodine species in the water sample are first oxidized to iodate (IO_3^{-1}) by sodium hypochlorite (NaClO), and then reduced to iodide (I^{-1}) by sodium bisulfite. The iodine is finally oxidized to molecular iodine (I_2) and extracted from most other radionuclides and elements in solution by a nonpolar organic solvent such as carbon tetrachloride (CCl_4) or chloroform ($CHCl_3$) (see Section 14.4, "Solvent Extraction").

Plutonium and its tracers can be equilibrated in a reproducible mixture of oxidation states by the rapid reduction of all forms of the ion to the +3 state, momentarily, with iodide ion (I^{-1}) in acid solution. Disproportionation begins immediately, but all radionuclide forms of the analyte and tracer begin at the same time from the same oxidation state, and a true equilibrium mixture of the radionuclide and its tracer is achieved. All plutonium radionuclides in the same oxidation state can be expected to behave the same chemically in subsequent separation and detection procedures.

In addition to dissolution and separation strategies, oxidation-reduction processes are used in several quantitation steps of radiochemical analyses. These processes include titration of the analyte and electrochemical deposition on a target for counting.

The classical titrimetric method is not commonly employed in the quantitation of environmental level samples because the concentrations of radionuclides in these samples are typically too low for detection of the endpoint of the titration, even by electrometric or spectroscopic means. However, the method is used for the determination of radionuclides in other samples containing larger quantities of long-lived radionuclides. Millimole quantities of uranium and plutonium in nuclear fuels have been determined by titration using methods of endpoint detection as well as chemical indicators (IAEA, 1972). In one method, uranium in the +6 oxidation state is reduced to +3 and +4 with Ti^{+3}, and that in the +3 state is oxidized to +4 with air bubbles (Baetsel and Demildt, 1972). The solution is then treated with a slight excess of Ce^{+4} solution of known concentration, which oxidizes U^{+4} to U^{+6} (as UO_2^{+2}) while being reduced, as follows:

$$U^{+4} + 2\ Ce^{+4} \rightarrow U^{+6} + 2\ Ce^{+3}$$

$$(U^{+4} + 2\ Ce^{+4} + 2\ H_2O \rightarrow UO_2^{+2} + 2\ Ce^{+3} + 4\ H^{+1})$$

The excess Ce^{+4} is back-titrated with Fe^{+2} solution, using ferrion as indicator for the endpoint of the titration:

$$Fe^{+2} + Ce^{+4} \rightarrow Fe^{+3} + Ce^{+3}$$

Electrochemical methods are typically used in radiochemistry to reduce ions in solution, plating them onto a target metal for counting. Americium ions (Am^{+3}) from soil samples are ultimately reduced from solution onto a platinum (Pt) electrode by application of an electrical current in an electrolytic cell (DOE, 1990 and 1997, Method Am-01). The amount of americium on the electrode is determined by alpha spectrometry.

In some cases, the deposition process occurs spontaneously without the necessity of an applied current. Polonium (Po) and lead (Pb) spontaneously deposit from a solution of hydrochloric acid (HCl) onto a nickel (Ni) disk at 85 °C (Blanchard, 1966). Alpha and beta counting are used to determine ^{210}Po and ^{210}Pb. Wahl and Bonner (1951, pp. 460-465) contains a table of electrochemical methods used for the oxidation and reduction of carrier-free tracers.

14.3 Complexation

14.3.1 Introduction

A *complex ion* is formed when a metal atom or ion bonds with one or more molecules or anions through an atom capable of donating one or more electron pairs. A *ligand* is any molecule or ion that has at least one electron pair that can be donated to the metal. The bond is called a *coordination bond*, and a compound containing a complex ion is a *coordination compound*. The following are several examples of the formation of complex ions:

$$Th^{+4} + 2\ NO_3^{-1} \rightarrow Th(NO_3)_2^{+2}$$

$$Ra^{+2} + EDTA^{-4\,*} \rightarrow Ra(EDTA)^{-2}$$

$$U^{+4} + 5\ CO_3^{-2} \rightarrow U(CO_3)_5^{-6}$$

* $EDTA^{-4}$ = Ethylenediaminetetraacetate, $(^{-1}OOC)_2\text{-}NH\text{-}CH_2\text{-}CH_2\text{-}NH\text{-}(COO^{-1})_2$

In a fundamental sense, every ion in solution can be considered complexed; there are no free or "naked" ions. Dissolved ions are surrounded by solvent molecules. In aqueous solutions, the

complexed water molecules, referred to as the *inner hydration sphere*, form aquo ions that can be either weakly or strongly bound:

$$Fe^{+2} + 6\ H_2O \rightarrow Fe(H_2O)_6^{+2}$$

From an elementary standpoint, the process of complexation is simply the dynamic process of replacing one set of ligands, the solvent molecules, with another. The complexation of a metal ion in aqueous solution with a ligand, L, can be expressed as:

$$M(H_2O)_n^{+x} + L^{-y} \rightarrow M(H_2O)_{n-1}L^{x-y} + H_2O$$

Successive aquo groups can be replaced by other ligand groups until the complex ML_n^{x-ny} is formed as follows:

$$M(H_2O)_{n-1}L + L \rightarrow M(H_2O)_{n-2}L_2 + H_2O, \text{ etc.}$$

In the absence of other complexing agents, in dilute aqueous solution solvated metal ions are simply written as M^{+n} for simplicity.

Ligands are classified by the number of electrons they donate to the metal to form coordination bonds to the metal. If only one atom in the ligand is bonded to the metal, it is called a unidentate ligand (*dentate* is from the Latin word for teeth. It is a categorization of ligands that describe the number of atoms with electron pairs a ligand has available for donation in complex-ion formation; if two atoms, bidentate, and so on for tridentate, tetradentate, pentadentate, and hexadentate.) The term *coordination number* is also used to indicate the number of atoms donating electrons to the metal atom. The coordination number is five in $U(CO_3)_5^{-6}$, as illustrated above. EDTA, also illustrated above, is a hexadentate ligand, because it bonds to the metal through the four oxygen atoms and two nitrogen atoms.

Table 14.4 lists some common ligands arranged by type.

TABLE 14.4 — Common ligands

Ligand Type [1]	Examples
Unidentate	Water (H_2O), halides (X^{-1}), hydroxide (OH^{-1}), ammonia (NH_3), cyanide (CN^{-1}), nitrite (NO_2^{-1}), thiocyanate (SCN^{-1}), carbon monoxide (CO)
Bidentate	Oxalate, ethylenediamine, citrate
Tridentate	Diethylenetriamine, 1,3,5 triaminocyclohexane

Ligand Type (1)	Examples
Polydentate	8-hydroxyquinoline, β-diketones (acetylacetone-2-thenoyltrifluoroacetone [TTA]), ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA), organophosphates: (octyl(phenyl)-*N*,*N*-diiso-butylcarbamoyl-methylphosphine oxide [CMPO]); tributyl phosphate (TBP), trioctylphosphinic oxide (TOPO), quaternary amines (tricaprylyl-methylammonium chloride [Aliquat-336]), triiso-octylamine (TIOA), tri-n-octylamine (TnOA), macrocyclic polyethers (crown ethers such as [18]-crown-6), cryptates

(1) Ligands are categorized by the number of electron pairs available for donation. Unidentate ligands donate one pair of electrons; bidentate donate two pairs, etc.

A ligand can be characterized by the nature and basicity of its ligand atom. Oxygen donors and the fluoride ion are general complexing agents; they combine with any metal ion (cation) with a charge of more than one. Acetates, citrates, tartrate, and β-diketones generally complex all metals. Conversely, cyanide (CN^{-1}), the heavy halides, sulfur donors, and—to a smaller extent—nitrogen donors, are more selective complexing agents than the oxygen donors. These ligands do not complex the A-metals of the periodic table; only the cations of the B-metals and the transition metals coordinate to carbon, sulfur, nitrogen, chlorine, bromine, and iodine.

14.3.2 Chelates

When a multidentate ligand is bound to the metal atom or ion by two or more electron pairs, forming a ring structure, it is referred to as a *chelate* and the multidentate ligand is called a chelating agent or reagent. Chelates are organic compounds containing two, four, or six carboxylic acid (RCOOH) or amine (RNH_2) functional groups. A chelate is effective at a pH where the acid groups are in the anionic form as carboxylates, $RCOO^{-1}$, but the nitrogen is not protonated so that its lone pair of electrons is free for bonding. The chelate bonds to the metal through the lone pair of electrons of these groups as bi, tetra, or hexadentate ligands, forming a coordination complex with the metal. Binding through multiple sites wraps up the metal in a claw-like fashion, thus the name chelate, which means claw. Practically all chelates form five- or six-membered rings on coordinating with the metal. Chelates are much more stable than complex compounds formed by unidentate reagents. Moreover, if multiple ring systems are formed with a single metal atom or ion, stability improves. For example, ethylenediaminetetraacetic acid (EDTA), a hexadentate ligand, forms especially stable complexes with most metals. As illustrated in Figure 14.1, EDTA has two donor pairs from the nitrogen atoms, and four donor pairs from the oxygen atoms.

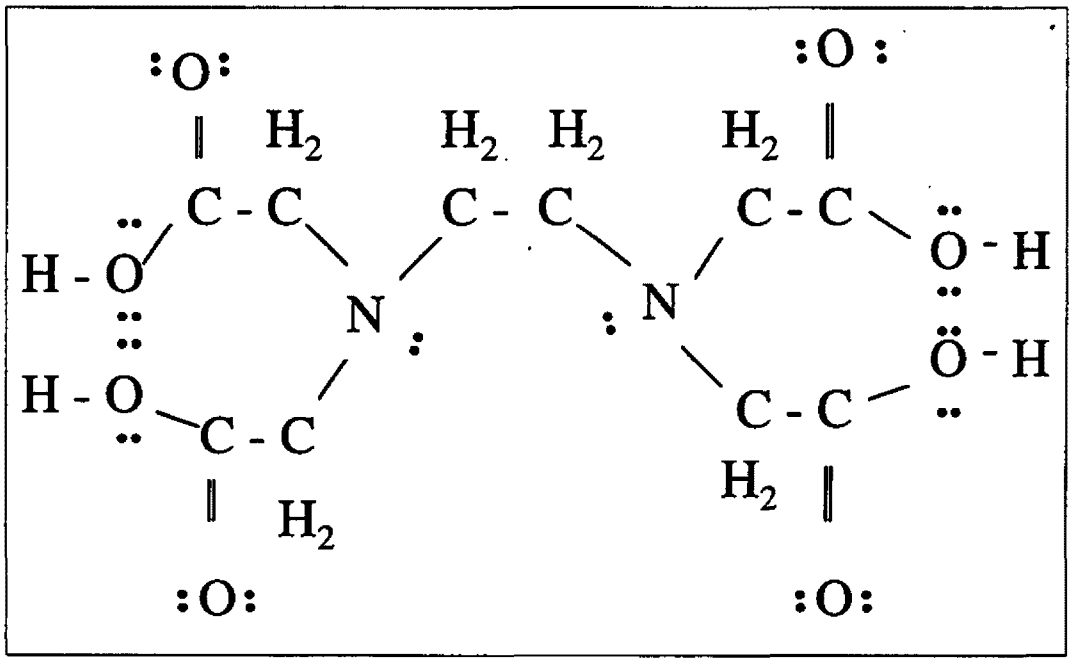


FIGURE 14.1 — Ethylenediaminetetraacetic Acid [1] (EDTA)

(1) EDTA forms very stable complexes with most metal atoms because it has two pairs of electrons available from the nitrogen atoms, and four pairs of electrons from the oxygen atoms. It is often used as a complexing agent in a basic solution. Under these conditions, the four carboxylic-acid groups ionize with the loss of a hydrogen ion (H^{+1}), forming ethylenediaminetetraacetate ($EDTA^{-4}$), a stronger complexing agent. EDTA is often used as a food additive to increase shelf life, because it combines with transition metal ions that catalyze the decomposition of food. It is also used as a water softener to remove calcium (Ca^{+2}) and magnesium (Mg^{+2}) ions from hard water.

Various chelating agents bind more readily to certain cations, providing the specificity for separating ions by selective bonding. Usually, the complex is insoluble under the solvent conditions used, allowing the collection of the complex by precipitation. Selectivity of a chelate can be partially controlled by adjusting the pH of the medium to vary the net charge on its functional groups. Different chelates provide specificity through the number of functional groups available for bonding and the size of claw formed by the molecular structure, providing a select fit for the diameter of a specific cation. The electron-donating atoms of the chelate form a ring system with the metal atom when they participate in the coordination bond. In most cases, chelates form much more stable complexes than unidentate ligands. For example, the complex ion formed between Ni^{+2} and the bidentate ligand ethylenediamine ($H_2N\text{-}CH_2\text{-}CH_2\text{-}NH_2$, or en), $Ni(en)_3^{+2}$, is almost 10^8 times more stable than the complex ion formed between the metal ion and ammonia, $Ni(NH_3)^{+2}$.

574 Another class of ligands that is becoming increasingly important to the radiochemist doing
575 laboratory analyses is the macrocyclic polyethers, commonly called *crown ethers* (Horwitz et al.,
576 1991 and 1992; Smith et al., 1996 and 1997). These compounds are cyclic ethers containing a
577 number of regularly spaced oxygen atoms. Some examples are given in Figure 14.2.

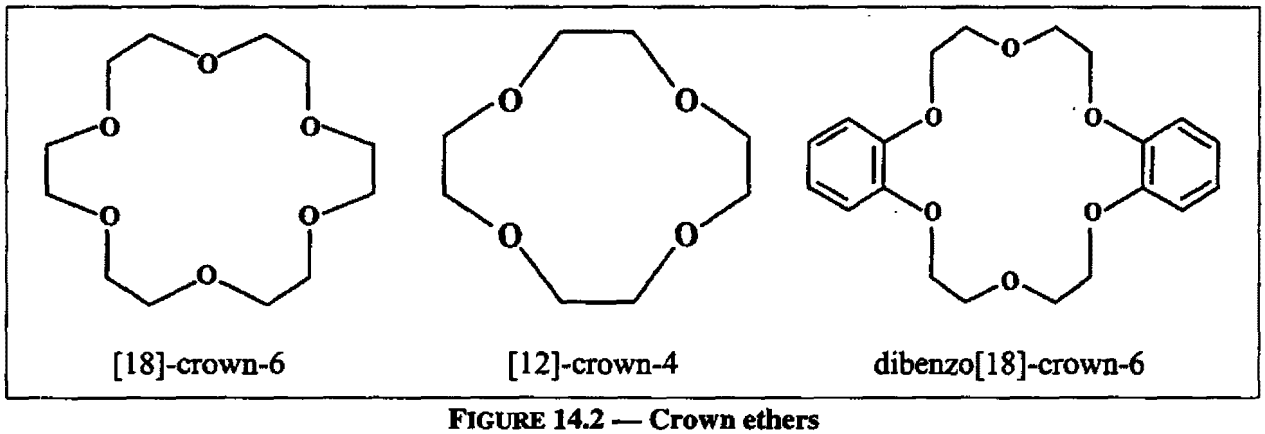


FIGURE 14.2 — Crown ethers

578 First identified in 1967, crown ethers have been shown to form particularly stable coordination
579 complexes. The term, "crown ether," was suggested by the three-dimensional shape of the
580 molecule. In the common names of the crown ethers, the ring size is given in brackets, and the
581 number of oxygen atoms follows the word "crown."

582 Crown ethers have been shown to react rapidly and with high selectivity (Gokel, 1991; Hiraoka,
583 1992). This property is particularly significant when a separation requires high selectivity and
584 efficiency in removing low-level species from complex and concentrated matrices, a situation
585 frequently encountered in environmental or mixed-waste analyses. Because crown ethers are
586 multidentate chelating ligands, they have very high formation constants. Moreover, because the
587 metal ion must fit within the cavity, crown ethers demonstrate some selectivity for metal ions
588 according to their size. Crown ethers can be designed to be very selective by changing the ring
589 size, the ring substituents, the ring number, the donor atom type, etc. For example, dibenzo-18-
590 crown-6 forms a strong complex with potassium; weaker complexes with sodium, cesium, and
591 rubidium; and no complex with lithium or ammonium, while 12-crown-4, with its smaller cavity,
592 specifically complexes with lithium.

593 Other crown ethers are selective for radionuclide ions such as radium and UO_2^{+2}. Addition of 18-
594 crown-6 to solutions containing NpO_2^{+2} causes the reduction of neptunium to Np(V) as NpO_2^{+1},
595 which is encircled by the ether ligand (Clark et al., 1998).

14.3.3 The Formation (Stability) Constant

The stability of the complex is represented by the magnitude of an equilibrium constant representing its formation. The complex ion, $[Th(NO_3)_2^{+2}]$, forms in two equilibrium steps:

$$Th^{+4} + NO_3^{-1} \rightarrow Th(NO_3)^{+3}$$

$$Th(NO_3)^{+3} + NO_3^{-1} \rightarrow Th(NO_3)_2^{+2}$$

The *stepwise formation (stability) constants* are:

$$K_1 = \frac{[Th(NO_3)^{+3}]}{[Th^{+4}][NO_3^{-1}]}$$

and

$$K_2 = \frac{[Th(NO_3)_2^{+2}]}{[Th(NO_3)^{+3}][NO_3^{-1}]}$$

The *overall formation (stability) constant* is:

$$K = \frac{[Th(NO_3)_2^{+2}]}{[Th^{+4}][NO_3^{-1}]^2}$$

which can be calculated from K_1 and K_2:

$$K = K_1 \times K_2.$$

In the Ni^{+2} examples cited in the preceding section, the relative stabilities of the complex ions are represented by the values of K; for $Ni(en)_3^{+2}$ it is $10^{18.28}$, and for $Ni(NH_3)^{+2}$ it is $10^{8.61}$ (Cotton and Wilkinson, 1988, p. 45).

Many radionuclides form stable complex ions and coordination compounds that are important to the separation and determination steps in radioanalytical chemistry. Formation of a complex changes the properties of the ion in several ways. For example:

- Complexation of UO_2^{+2} with carbonate to form $UO_2(CO_3)^{-4}$ increases the solubility of the uranium species in groundwater (Lindsay, 1988, p. 9.2-19).

- Th^{+2} forms $Th(NO_3)_6^{-2}$ in nitric acid solution (optimally at 7 M) that is the basis for separation of thorium from other actinides and thorium progeny, because they do not form anionic complexes under these conditions (Hyde, 1960, p. 25).

- Ra^{+2} form a very insoluble compound with sulfate ($RaSO_4$) but is soluble in hot concentrated sulfuric acid because of the formation of $Ra(SO_4)_2^{-2}$ (Kirby and Salutsky, 1964, p. 9).

In addition, the complex ion in solution is in equilibrium with the free (hydrated) ion, and the equilibrium mixture might, therefore, contain sufficient concentration of the free ion for it to be available for other reactions, depending on the stability of the complex ion:

$$Cu^{+2} + 4\ NH_3 \rightarrow Cu(NH_3)_4^{+2}$$

14.3.4 Complexation and Radiochemical Analysis

Property changes also accompany the formation of complex ions and coordination compounds from simple radionuclide ions. These changes provide a valuable approach in radiochemistry for isolating, separating, and measuring radionuclide concentrations, and are important in several areas of radiochemistry.

14.3.4.1 Extraction of Laboratory Samples and Ores

Uranium ores are leached with alkaline carbonates to dissolve uranium as the $UO_2(CO_3)_2^{-4}$ complex ion after oxygen is used to convert U^{+4} to U^{+6} (Grindler, 1962, p. 256). Samples containing refractory plutonium oxides are dissolved with the aid of a nitric acid-hydrofluoric acid solution to produce the complex cation PuF^{+3} and similar cationic fluorocomplexes (Booman and Rein, 1962, p. 244). Refractory silicates containing niobium (Nb) also yield to fluoride treatment. Potassium bifluoride (KF_2^{-1}) is used as a low-temperature flux to produce a fluoride complex NbF_6^{-1} (Willard and Rulfs, 1961, p. 1046; Greenwood and Earnshaw, 1984, p. 1158).

14.3.4.2 Separation by Solvent Extraction and Ion-Exchange Chromatography

Many ion-exchange separations of radionuclides are based on the formation of complex ions from the metal ions in solution or the displacement of ions bound to an exchanger by complex formation. Uranium in urine samples, for example, is partly purified by forming a chlorocomplex of U^{+4} and UO_2^{+2} ions, UCl_6^{-2} and $UO_2Cl_3^{-1}$, that bind preferentially to the anion-exchange ligands

in 7 M HCl. Other cations pass through the column under these conditions. Uranium is subsequently eluted with 1 M HCl (DOE, 1990 and 1997, Method U-01).

For separation on a larger scale—such as in an industrial setting—chelates are often used in a column chromatography or filtration unit. They are immobilized by bonding to an inert matrix, such as polystyrene or an alumina/silica material. A solution containing the ions to be separated is passed continuously through the column or over the filter, where the select cations are bonded to the chelate as the other ions pass through. Washing the column or filter with a solution at alternate pH or ionic strength will permit the elution of the bound cation.

Tetrapositive thorium (Th) is adsorbed more strongly by cation exchangers than most other cations (Hyde, 1960, pp. 21-23). The adsorbed thorium is separated from most other ions by washing the column with mineral acids or other eluting agents. Even the tetrapositive plutonium ion, Pu^{+4}, and the uranyl ion, UO_2^{+2}, are washed off with high concentrations of HCl because they form chlorocomplexes, $PuCl_6^{-2}$ and $UO_2Cl_3^{-1}$, respectively. Thorium is then removed by eluting with a suitable complexing agent such as oxalate, which reduces the effective concentration of Th^{+4}, reversing the adsorption process. Using oxalate, $Th(C_2O_4)_4^{-4}$ forms and the anion is not attracted to the cation exchanger.

14.3.4.3 Formation and Dissolution of Precipitates

A classical procedure for the separation and determination of nickel (Ni) is the precipitation of Ni^{+2} with dimethylglyoxime, a bidentate ligand that forms a highly selective, stable chelate complex with the ion, $Ni(C_4H_7N_2O_2^{-1})_2$ (DOE, 1995, Method RP300). Uranium in the +4 oxidation state can also be precipitated from acidic solutions with a chelating agent, cupferron (ammonium nitrosophenylhydroxylamine, $C_8H_5(NO)O^{-1}NH_4^{+1}$) (Grindler, 1962, p. 256). In another procedure, Co^{+2} can be selectively precipitated from solution as $K_3Co(NO_2)_6$. In this procedure, cobalt, which forms the largest number of complexes of all the metals, forms a complex anion with six nitrite ligands, $Co(NO_2)_6^{-3}$ (EPA, 1973, pp. 53-58).

In radiochemical separations and purification procedures, precipitates of radionuclides are commonly redissolved to release the metal ion for further purification or determination. In the determination of ^{90}Sr, strontium (Sr^{+2}) is separated from the bulk of the solution by direct precipitation of the sulfate, $SrSO_4$. The precipitate is redissolved by forming a complex ion with EDTA, $Sr(EDTA)^{-2}$, to separate it from lanthanides and actinides (DOE, 1995, Method RP520). Radium also forms a very stable complex with EDTA. Solubilization of radium, Ra^{+2}, coprecipitated with barium sulfate ($BaSO_4$) is used in the ^{228}Ra determination of drinking water by using EDTA (EPA, 1980, pp. 49-57).

14.3.4.4 Stabilization of Ions in Solution

In some radiochemical procedures, select radionuclides are separated from other elements and other radionuclides by stabilizing the ions as complex ions, while the other substances are precipitated from solution. In a procedure extensively used at Oak Ridge National Laboratory (ORNL), ^{95}Nb is determined in solutions by taking advantage of complex-ion formation to stabilize the ion (Nb^{+5}) in solution during several steps of the procedure (Kallmann, 1964, pp. 343-344). The niobium sample and carrier are complexed with oxalic acid in acidic solution to prevent precipitation of the carrier and to promote interchange between the carrier and ^{95}Nb. Niobium is precipitated as the pentoxide after warming the solution to destroy the oxalate ion, separating it from the bulk of other ions in solution. Niobium is also separated specifically from zirconium by dissolving the zirconium oxide in hydrofluoric acid.

14.3.4.5 Detection and Determination

Complexiметric titration of metal ions with EDTA using colorimetric indicators to detect the endpoint can be used for determination procedures. Uranium does not form a selective complex with EDTA, but this chelate has been used to titrate pure uranium solutions (Grindler, 1962, p. 94). The soluble EDTA complex of thorium is the basis of a titrimetric determination of small amounts of thorium (Hyde, 1960, p. 9).

Spectrometric determinations are also based on the formation of complex ions. Microgram quantities of uranium are determined by the absorbance at 415 nm (a colorimetric determination) of the uranyl chelate complex with dibenzoylmethane, C_6H_5-CO-CH_2-CO-C_6H_5 (Grindler, 1962, pp. 271-276).

14.4 Solvent Extraction

14.4.1 Extraction Principles

Since the early days of the Manhattan Project, when scientists extracted uranyl nitrate into diethyl ether to purify the uranium used in the first reactors, solvent extraction has been an important separation technique for radiochemists. Solvent extraction, or liquid-liquid extraction, is a technique used both in the laboratory and on the industrial scale. However, current laboratory trends are away from this technique, mainly because of the costs of materials and because it is becoming more difficult and costly to dispose of the mixed waste generated from the large volumes of solvents required. The technique also tends to be labor intensive because of the need

for multiple extractions using separatory funnels. Nonetheless, solvent extraction remains a powerful separation technique worthy of consideration.

Solvent extraction refers to the process of selectively removing a solute from a liquid mixture with a solvent. As a separation technique, it is a partitioning process based on the unequal distribution of the solute (A) between two immiscible solvents, usually water (aq) and an organic liquid (org):

$$A_{aq} \rightleftharpoons A_{org}$$

The solute can be in a solid or liquid form. The extracting solvent can be water, a water-miscible solvent, or a water-immiscible solvent; but it must be insoluble in the solvent of the liquid mixture. Solutes exhibit different solubilities in various solvents. Therefore, the choice of extracting solvent will depend upon the properties of solute, the liquid mixture, as well as other requirements of the experimental procedure. The solvents in many applications are water and a nonpolar organic liquid, such as hexane or diethyl ether, but other solvent pairs are commonly used. In general terms, the solute to be removed along with impurities or interfering analytes to be separated are already dissolved in one of the solvents (water, for example). In this example, a nonpolar organic solvent is added and the two are thoroughly mixed, usually by shaking in a separatory funnel. Shaking produces a fine dispersion of each solvent in the other that will separate into two distinct layers after standing for several minutes. The more dense solvent will form as the bottom layer. Separation is achieved because the solute and accompanying impurities or analytes have different solubilities in the two solvents. The solute, for example, might preferentially remain in the aqueous phase, while the impurities or analyte selectively dissolve in the organic phase. The impurities and analyte are *extracted* from the aqueous layer into the organic layer. Alternatively, the solute might be more soluble in the organic solvent and will be extracted from the aqueous layer into the organic layer, leaving the impurities behind in the aqueous layer.

14.4.2 Distribution Coefficient

The different solubilities of a solute in the solvent pairs of an extraction system are described by the *distribution* or *partition coefficient*, K_d. The coefficient is an equilibrium constant that represents the solubility of the solute in one solvent relative to its solubility in another solvent. Once equilibrium is established, the concentration of solute in one phase has a direct relationship to the solute concentration in the other phase. This is expressed mathematically by:

$$K_d = [A_{org}] / [A_{aq}]$$

where $[A_{org}]$ and $[A_{aq}]$ are the concentration of the solute in the organic and aqueous phase respectively, and K_d is a constant. The concentrations are typically expressed in units of moles/kg (molality) or g/g; therefore, the constant is unitless. These solubilities usually represent saturated concentrations for the solute in each solvent. Because the solubilities vary with temperature, the coefficient is temperature-dependent, but not by a constant factor. Wahl and Bonner (1951, pp. 434-439) contains a table of solvent extraction systems for carrier-free tracers containing laboratory conditions and distribution coefficients.

A distribution coefficient of 90 for a solute in a hexane/water system, for example, means that the solute is 90 times more soluble at saturation conditions in hexane than in water, but note that some of the water still contains a small amount of the solute. Solvent extraction selectively dissolves the solute in one solvent, but it does not remove the solute completely from the other solvent. A larger coefficient would indicate that, after extraction, more solute would be distributed in hexane relative to water, but a small quantity would still be in the water. Solvent extraction procedures often use repeated extractions to extract a solute quantitatively from a liquid mixture.

The expression of the distribution law is only a very useful approximation; it is not thermodynamically rigorous, nor does it account for situations in which the solute is involved in a chemical reaction, such as dissociation or association, in either phase. Consider, for example, dimerization in the organic phase:

$$2A_{org} \rightleftharpoons (A)_{2,\,org}$$

where the distribution ratio, D, is an alternate form of the distribution coefficient expressed by:

$$D = ([A_{org}]_{monomer} + [A_{org}]_{dimer})/[A_{aq}]$$

or

$$D = ([A_{org}] + 2\,[(A)_{2,\,org}])\,/[A_{aq}]$$

Because the concentration of the monomer that represents the dimeric form of the solute is twice that of the concentration of the dimer:

$$[A_{org}]_{dimer} = 2[(A)_{2,\,org}]$$

Substitution of K_d produces:

$$D = K_d(1 + 2K_2\,[A_{org}])$$

where K_2 is the dimerization constant, $K_2 = [(A)_{2,org}]/[A_{org}]^2$. Because dimerization decreases the concentration of the monomer, the species that takes part directly in the phase partition, the overall distribution increases.

14.4.3 Extraction Technique

There is extensive literature on the topic of extraction technique, but only a few sources are listed here. The theory of solvent extraction is covered thoroughly in Irving and Williams (1961), Lo et al. (1983), and Dean (1995). Moreover, the journal *Solvent Extraction and Ion Exchange* is an excellent source for current advances in this field. A practical discussion on the basics of solvent extraction is found in Korkisch (1969). The discussion applies to a metallic element in solution as a cation extracted by a nonpolar solvent:

> "In solvent extraction, the element which is to be separated, contained in an aqueous solution, is converted to a compound which is soluble in an organic solvent. The organic solvent must be virtually immiscible with water. By shaking the aqueous solution with the organic solvent (extractant) in a separating funnel, the element is extracted into the organic phase. After allowing the aqueous and organic phases to separate in the funnel, the organic extract is removed from contact with the aqueous layer. This single-stage batch extraction method is employed when K_d is relatively large and for a simple separation it is essential that the distribution coefficients of the metal ions to be separated be sufficiently different. As in the case of ion exchange, the effectiveness of separation is usually expressed by means of the separation factor which is given by the ratio of the distribution coefficients of two different elements which were determined under identical experimental conditions. This ratio determines the separability of two elements by liquid-liquid extraction. Separations can only be achieved if this ratio shows a value which is different from unity and they are clean and can be quickly and easily achieved where one of the distribution coefficients is relatively large and the other very small (high separation factor).
>
> "In those extractions where the separation factor approaches unity, it is necessary to employ continuous extraction or fractionation methods. With the latter techniques distribution, transfer and recombination of various fractions are performed a sufficient number of times to achieve separation. In continuous extraction use is made of a continuous flow of immiscible solvent through the solution or a continuous counter-current flow of both phases. In continuous extraction the spent solvent is stripped and recycled by distillation, or fresh solvent is added continuously from a reservoir. Continuous counter-current extraction involves a process where the two liquid phases are caused to flow counter to each other. Large-scale separations are usually performed using this technique.

"When employing liquid-liquid extraction techniques, one of the most important considerations is the selection of a suitable organic solvent. Apart from the fact already mentioned that it must be virtually immiscible with water, the solubility of the extracted compound in the solvent must be high if a good separation is to be obtained. Furthermore, it has to be selective, i.e., has to show the ability to extract one component of a solution in preference to another. Although the selectivity of a solvent for a given component can be determined from phase diagrams, it is a little-used procedure in analytical chemistry. The principal difficulty is simply that too few phase diagrams exist in the literature. The result is that the choice of an extractant is based on either experience or semi-empirical considerations. As a rule, however, polar solvents are used for the extraction of polar substances from nonpolar media, and vice versa. Certainly the interactions of solute and solvent will have an effect on the selectivity of the solvent. If the solute is readily solvated by a given solvent, then it will be soluble in that solvent. Hydrogen bond formation between solute and solvent influences solubility and selectivity.

"Almost as important as the selectivity of the extractant is the recovery of the solute from the organic extract. Recovery can be achieved by distillation or evaporation of the solvent, provided that the solute is nonvolatile and thermally stable. This technique is, however, less frequently used than the principle of back extraction (stripping) which involves the treatment of the organic extract with an aqueous solution containing a reagent which causes the extracted solute to pass quantitatively into the aqueous layer...

"In solvent extraction the specific gravity of the extractant in relation to the aqueous phase is important. The greater the difference in the solvent densities, the faster will be the rate at which the immiscible layers separate. Emulsions are more easily produced when the densities of the two solvents are similar. Sometimes troublesome emulsions can be broken by introducing a strong electrolyte into the system or by the addition of small quantities of an aliphatic alcohol" (Korkisch, 1969, pp. 20-22).

Korkisch continues:

"Liquid-liquid extraction can be applied to the analysis of inorganic materials in two different ways.

(a) Where the element or elements to be determined are extracted into the organic phase.

(b) Where the interfering elements are removed by extraction, leaving the element or elements to be determined in the aqueous phase.

> "Solvent extraction separations are mainly dependent for their successful operation upon the distribution ratio of the species between the organic and aqueous phase and the pH and salt concentration of the aqueous phase. Much of the selectivity which is achieved in liquid-liquid extraction is dependent upon adequate control of the pH of the solution. The addition of masking agents such as EDTA and cyanide can greatly improve selectivity, but they too are dependent upon the pH of the solution to exert their full effect. In many cases complete extractions and separations are obtained only in the presence of salting-out agent. An example is the extraction of uranyl nitrate. In the presence of additional nitrate, the increase in the concentration of the nitrate ion in the aqueous solution shifts the equilibrium between the uranyl ion and the nitrate complexes toward the formation of the latter, and this facilitates a more complete extraction of the uranium into the organic solvent. At the same time, the salting-out agent has another, more general, effect: as its affinity for water is large, it becomes hydrated by the water molecules so that the substance to be extracted is really dissolved in a smaller amount of water, and this is the same as if the concentration in the solution were increased. As a result, the distribution coefficient between the aqueous and the organic phases is increased. As a rule the salting-out agent also lowers the solubility of the extractant in the aqueous phase, and this is often important in separations by extraction. The efficiency of the salting-out action depends upon the nature and the concentration of the salting-out agent. For the same molar concentration of the salting-out agent its action increases with an increase in the charge and decrease in the radius of its cation" (Korkisch, 1969, pp. 23-24).

A hydrated metal ion will always prefer the aqueous phase to the organic phase because of hydrogen bonding and dipole interaction in the aqueous phase. Therefore, to get the metal ion to extract, some or all of the inner hydration sphere must be removed. The resulting complex must be neutrally charged and organophilic. Removal of the hydration sphere is accomplished by coordination with an anion to form a neutral complex. Neutral complexes will generally be more soluble in an organic phase. Larger complexing anions favor the solubility in the organic phase.

Extracting agents are thus divided into three classes: polydentate organic anions, neutral organic molecules, and large organic cations. Many of the multidentate ligands discussed previously are used in solvent extraction systems.

The radioanalytical procedure for uranium (U) and thorium (Th) employs solvent extraction to separate the analytes before alpha counting (EPA, 1984, pp. U/Th-01-1-14). An aqueous solution of the two is extracted with a 10 percent solution of triisooctylamine (TIOA) in *para*-xylene to remove uranium, leaving thorium in the water (Grinder, 1962, pp. 175-180). Each solution is further processed to recover the respective radionuclides for separate counting.

14.4.4 Solvent Extraction and Radiochemical Analysis

In many purification procedures, separated solutions are used directly in further isolation steps. If necessary, the substances can be collected by distillation or evaporation of the respective solvents. In the uranium/thorium procedure described above, the aqueous layer containing thorium is evaporated, and the thorium is redissolved in an alternate solution before it is purified further. In other cases, the solution is extracted again to take up the solute in another solvent before the next step in the procedure. Uranium in TIOA/*p*-xylene, for example, is extracted back into a nitric acid solution for additional purification (EPA, 1984, pp. U/Th-01-1-U/Th-01-14).

In some solvent-extraction procedures, more than one extraction step is required for the quantitative removal of a solute from its original solvent. The solute is more soluble in one component of the solvent pair, but not completely insoluble in the other component, so successive extractions of the aqueous solution of the solute by the organic solvent will remove more and more of the solute from the water until virtually none remains in the aqueous layer. Extraction of uranium with TIOA/*p*-xylene, for example, requires two extractions before quantitative removal is achieved (EPA, 1984, pp. U/Th-01-1-U/Th-01-14). The organic layers containing the uranium are then combined into one solution for additional processing.

Solvent extraction is greatly influenced by the chemical form (ionic or molecular) of the solute to be extracted, because different forms of the solute can have different solubilities in the solvents. In the uranium/thorium procedure described above, uranium is extracted from water by TIOA/hydrochloric acid, but it is stripped from the amine solution when extracted with nitric acid. Simply changing the anion of uranium and TIOA from chloride to nitrate significantly alters the complex stability of uranium and TIOA.

Organic amines are sometimes converted to their cationic forms, which are much more soluble in water and much less soluble in organic solvents. The amine is converted to the corresponding ammonium salt by an acid, such as hydrochloric acid:

$$RNH_2 + HCl \rightarrow RNH_3^{+1}Cl^{-1}$$

Correspondingly, carboxylic acids are converted to their carboxylates that are more soluble in water and less soluble in organic solvents. They are produced by treating the carboxylic acid with a base, such as sodium hydroxide:

$$RCOOH + NaOH \rightarrow RCOO^{-1}Na^{+1} + H_2O$$

Multidentate organic anions that form chelates are important extracting agents. These reagents, such as the β-diketonates and thenoyltrifluoroacetone (TTA) (Ahrland, 1986, pp. 1518-1521), are commonly used for extracting the actinide elements. When the aqueous solution and organic phase come into contact with one another, the chelating agent dissolves in the aqueous phase, ionizes, and complexes the metal ion; the resulting metal chelate subsequently dissolves in the organic phase.

A number of organophosphorus compounds are also efficient extractants because they and their complexes are readily soluble in organic solvents. The actinide MO_2^{+2} and actinide +4 ions are very effectively extracted by reagents such as monobasic diethylhexylphosphoric acid (HDEHP) and dibutylphosphoric acid (HDBP) (Cadieux and Reboul, 1996).

Among the neutral compounds, alcohols, ethers, and ketones have been commonly employed as extractants. Methyl isobutyl ketone was used in one of the early large-scale processes (the Redox process) to recover uranium and plutonium from irradiated fuel (Choppin et al., 1995, p. 607). However, the most widely used neutral extractants are the organophosphorus compounds such as TBP (tributyl phosphate). The actinide elements thorium, uranium, neptunium, and plutonium easily form complexes with TBP (Choppin et al., 1995, p. 607). Salting-out agents such as HNO_3 and $Al(NO_3)_3$ are commonly employed to increase extraction in these systems. This chemistry is the basis of the Purex process used to reprocess spent nuclear fuel (Choppin et al., 1995, pp. 608-610).

An important addition to the Purex process is the solvent extraction procedure known as TRUEX (*Tr*ans *U*ranium *Ex*traction). This process uses the bifunctional extractant CMPO ([octyl(phenyl)]-N,N-diisobutylcarbonylmethylphosphine oxide) to remove transuranium elements from the waste solutions generated in the Purex process. This type of compound extracts actinides at high acidities, and can be stripped at low acidity or with complexing agents. Many of the recent laboratory procedures for biological waste and environmental samples are based upon this approach (see Section 14.4.5.1, "Extraction Chromatography Columns").

The amines, especially the tertiary and quaternary amines, are strong cationic extractants. These strong bases form complexes with actinide metal cations. The extraction efficiency improves when the alkyl groups have long carbon chains, such as in trioctylamine (TnOA) or triisooctylamine (TIOA). The pertechnetate ion (TcO_4^{-1}) is also extracted by these cationic extractants (Chen, 1990).

Table 14.5 lists common solvent extraction procedures for some radionuclides of interest and includes the examples described above.

933 **TABLE 14.5 — Radioanalytical methods employing solvent extraction (1)**

934 Analyte	Extraction Conditions (Reference)
935 $^{89/90}Sr$	From soils and sediments with dicyclohexano-18-crown-6 in trichloromethane with back extraction with EDTA (Pimpl, 1995)
936 $^{99}TcO_4^-$	From dilute H_2SO_4 solutions into a 5% TnOA in xylene mixture and back extracted with NaOH (Golchert and Sedlet, 1969; Chen, 1990); from dilute H_2SO_4, HNO_3, and HCl solutions into a 5% TnOA in xylene (Dale et al., 1996); from HNO_3 into 30% TnOA in xylene and back extracted with NaOH (Hirano, 1989); from dilute H_2SO_4 solutions into TBP (Holm et al., 1984; Garcia-Leon, 1990); the tetraphenyl arsonium complex of Tc into chloroform (Martin and Hylko, 1987); from K_2CO_3 with MEK (Paducah R-46); from alkaline nuclear-waste media with crown ethers (Bonnesen et al., 1995)
937 ^{210}Pb	As lead bromide from bone, food, urine, feces, blood, air, and water with Aliquat-336 (DOE, 1990 and 1997, Method Pb-01; Morse and Welford, 1971)
938 Radium through 939 Californium	From soil following KF-pyrosulfate fusion and concentration by barium sulfate precipitation with Aliquat-336 in xylene (Sill et al., 1974)
940 Actinides	From water following concentration by ferric hydroxide precipitation and group separation by bismuth phosphate precipitation, uranium extracted by TOPO, plutonium and neptunium extracted by TIOA from strong HCl, and thorium separated from americium and curium by extraction with TOPO (EPA, 1980, Method 907.0)
	And other metals from TOPO (NAS-NS 3102) and from high-molecular weight amines such as TIOA (NAS-NS 3101).
	Uranium and plutonium from HCl with TIOA (Moore, 1958)
	From nitric acid wastes using the TRUEX process with CMPO (Horwitz et al., 1985 and 1987)
	With various extractive scintillators followed by PERALS® spectrometry (McDowell 1986 and 1992); with HDEHP after extraction chromatography followed by PERALS® spectrometry (Cadieux and Reboul, 1996)
941 Thorium	From aqueous samples after ion exchange with TTA, TIOA, or Aliquat-336 (DOE, 1995, Method RP570)
942 Uranium	From waters with ethyl acetate and magnesium nitrate as salting-out agent (EPA, 1980, Method 908.1); with URAEX™ followed by PERALS® spectrometry (Leyba et al., 1995)
	From soil, vegetation, fecal ash, and bone ash with Alamine-336 (DOE, 1990 and 1997, Methods Se-01, U-03)

943 (1) This list is representative of the methods found in the literature. It is not an exhaustive compilation, nor does it
944 imply preference over methods not listed.

945 ### 14.4.5 Solid-Phase Extraction

946 A technique closely related to solvent extraction is solid-phase extraction (SPE). SPE is a
947 solvent-extraction system in which one of the liquid phases is made stationary by adsorption onto
948 a solid support, usually silica, and the other liquid phase is mobile. Small columns or membranes

are used in the SPE approach. Many of the same extracting agents used in solvent extraction can be used in these systems. SPE is becoming widely accepted as an excellent substitute for liquid-liquid extraction because it is generally faster, more efficient, and generates less waste.

14.4.5.1 Extraction Chromatography Columns

Over the past decade, *extraction chromatography* methods have gained wide acceptance in the radiochemistry community as new extraction chromatographic resins have become commercially available, such as Sr, TRU, and TEVA resins (Eichrom Industries, Inc., Darien, IL) (Dietz and Horwitz, 1993; Horwitz et al., 1991, 1992, and 1993). These resins are composed of extractant materials, such as CMPO and 4,4'(5')-bis(t-butylcyclohexano)-18-crown-6, absorbed onto an inert polymeric support matrix. They are most frequently used in a column, rather than a batch mode.

Another example of the advances in the area are use of fibrous discs impregnated with high molecular weight chelates, selective for certain nuclides such as Cs, Sr, and Tc (Empore Discs, 3M Company, and the TEVA Disc, Eichrom Industries, Inc.). Many of the traditional methods based upon repetitive precipitations, or solvent extraction in separatory funnels, have been replaced by this strategy. This approach allows for the specificity of liquid-liquid extraction with the convenience of column chromatography. Numerous papers detailing the determination of radionuclides by this technique have been published recently, and examples are cited in Table 14.6.

TABLE 14.6 — Radioanalytical methods employing extraction chromatography [1]

Analyte	Ligand	Method Citations
Ni-59/63	dimethylgloxime	Aqueous samples (DOE, 1997)
Sr-89/90	4,4'(5')-bis(t-butyl-cyclohexano)-18-crown-6 in n-octanol	Biological, Environmental, and Nuclear Waste (Horwitz et al., 1991 and 1992); Water (ASTM, D5811-95; DOE, 1995, Method RP500); Urine (Dietz and Horwitz, 1992; Alvarez and Navarro, 1996); Milk (Jeter and Grob, 1994); Geological Materials (Pin and Bassin, 1992)
Sr-90	octyl(phenyl)-*N*,*N*-diisobutyl-carbamoylmethylphosphine oxide [CMPO] in tributyl phosphate	Brines (Bunzl et al., 1996)
Y-90	4,4'(5')-bis(t-butyl-cyclohexano)-18-crown-6 in n-octanol	Medical applications (Dietz and Horwitz, 1992)
Tc-99	Aliquat-336N	Low-level radioactive waste (Banavali, 1995); Water (Sullivan et al., 1993; DOE, 1993, Method RP550)

Analyte	Ligand	Method Citations
Pb-210	4,4'(5')-bis(t-butyl-cyclohexano)-18-crown-6 in isodecanol	Water (DOE, 1995, Method RP280); Geological materials (Horwitz et al., 1994; Woittiez and Kroon, 1995); complex metal ores (Gale, 1996)
Ra-228	octyl(phenyl)-*N,N*-diisobutyl-carbamoylmethylphosphine oxide [CMPO] in tributyl phosphate or diethylhexyl-phosphoric acid [HDEHP] impregnated in Amberlite XAD-7	Natural waters (Burnett et al., 1995); Volcanic rocks (Chabaux, 1994)
Rare earths	diamyl,amylphosphonate	Actinide-containing matrices (Carney, 1995)
	octyl(phenyl)-*N,N*-diisobutyl-carbamoylmethylphosphine oxide [C-MPO] in tributyl phosphate and dieth ylhexyl-phosphoric acid [HDEHP] impregnated in Amberlite XAD-7	Sequential separation of light rare earths, U, and Th in geological materials (Pin et al., 1996)
	octyl(phenyl)-*N,N*-diisobutyl-carbamoylmethylphosphine oxide [CMPO] in tributyl phosphate and 4,4'(5')-bis(t-butyl-cyclohexano)-18-crown-6 in n-octanol	Concomitant separation of Sr, Sm, and Nd in silicate samples (Pin et al., 1994)
Actinides	octyl(phenyl)-*N,N*-diisobutyl-carbamoylmethylphosphine oxide [CMPO] in tributyl phosphate	Air filters (Berne, 1995); Waters (Berne, 1995); Group-screening (DOE, 1997, Method RP725); Urine (Horwitz et al., 1990; Nguyen et al., 1996); Acidic media (Horwitz, 1993; DOE, 1997); Soil and sludge (Smith et al., 1995; Kaye et al., 1995); Environmental (Bunzl and Kracke, 1994)
	diamyl,amylphosphonate	Acidic media (Horwitz et al., 1992)
	tri-n-octylphosphine oxide [TOPO] and di(2-ethylhexyl)phosphoric acid [HDEHP]	Environmental and industrial samples (Testa et al., 1995)

(1) This list is representative of the methods found in the literature. It is not complete, nor does it imply preference over methods not listed.

14.4.5.2 Extraction Membranes

SPE membranes have also become a popular approach to sample preparation for organic compounds in aqueous samples over the past decade. As of 1995, 22 methods employing SPE disks have been accepted by the U.S. Environmental Protection Agency. More recently, disks have been developed for specific radionuclides, such as technetium, strontium, and radium (DOE, 1990 and 1997; Orlandini, 1998; Smith et al., 1996 and 1997).

These SPE membranes significantly reduce extraction time and reagent use. Samples typically are processed through the membranes at flow rates of at least 50 milliliters per minute; a one liter sample can be processed in as little as 20 minutes. Moreover, these selective-membranes often can be counted directly, thereby condensing sample preparation and counting source preparation into a single step. Many of the hazardous reagents associated with more traditional methods are eliminated in this approach, and these membrane-based extractions use up to 90 percent less solvent than liquid-liquid extractions. The sorbent particles embedded in the membrane are extremely small and evenly distributed, thereby eliminating the problem of channeling that is associated with columns.

14.4.6 Advantages and Disadvantages of Solvent Extraction

14.4.6.1 Advantages

- Lends itself to rapid and very selective separations that are usually highly efficient.
- Partition coefficients are often approximately independent of concentration down to tracer levels and, therefore, can be applied to a wide range of concentrations.
- Can usually be followed by back-extraction into aqueous solvents or, in some cases, the solution can be used directly in subsequent procedures.
- Wide scope of applications—the composition of the organic phase and the nature of complexing or binding agents can be varied so that the number of practical combinations is virtually unlimited.
- Can be performed with simple equipment, but can also be automated.
- Column extraction is fast, very selective, generates a low volume of waste, can often be applied to samples from very acidic media, requires relatively inexpensive materials, and can often be correlated with liquid/liquid extraction.

14.4.6.2 Disadvantages

- Cumbersome for a large number of samples or for large samples.
- Often requires toxic and/or flammable solvents.

- Can be time consuming, especially if attainment of equilibrium is slow.
- Can require costly amounts of organic solvents and generate large volumes of organic waste.
- Can be affected by small impurities in the solvent(s).
- Multiple extractions might be required, thereby increasing time, consumption of materials, and generation of waste.
- Formation of emulsions can interfere.
- Counter-current process can be complicated and can require complicated equipment.
- Alteration of chemical form can change, going from one phase to the other, thereby altering the distribution coefficient and effectiveness of the extraction.
- Tracer-levels of analytes can form radiocolloids that cannot be extracted, dissociate into less soluble forms, or adsorb on the container surface or onto impurities in the system.
- Extraction columns cannot be reused.

14.5 Volatilization and Distillation

14.5.1 Introduction

Differences in vapor pressures of elements or their compounds can be exploited for the separation of radionuclides. Friedlander et al. (1981, p. 300), describes the process:

> "The most straightforward application is the removal of radioactive rare gases from aqueous solutions or melts by sweeping an inert gas or helium. The volatility of ... compounds ... can be used to effect separations ...by distillation ... Distillation and volatilization methods often give clean separations, provided that proper precautions are taken to avoid contamination of the distillate by spray or mechanical entrapment. Most volatilization methods can be done without specific carriers, but some nonisotopic carrier gas might be required. Precautions are sometimes necessary to avoid loss of volatile radioactive substances during the dissolving of irradiated targets or during irradiation itself."

Similar precautions are also advisable during the solubilization of samples containing volatile elements or compounds (Chapter 13, *Sample Dissolution*).

14.5.2 Volatilization Principles

Volatilization particularly provides a rapid and often selective method of separation for a wide range of elements (McMillan, 1975, p. 306). A list of the elements that can be separated by volatilization and their chemical form(s) upon separation are given in Table 14.7 (McMillan, 1975, p. 307).

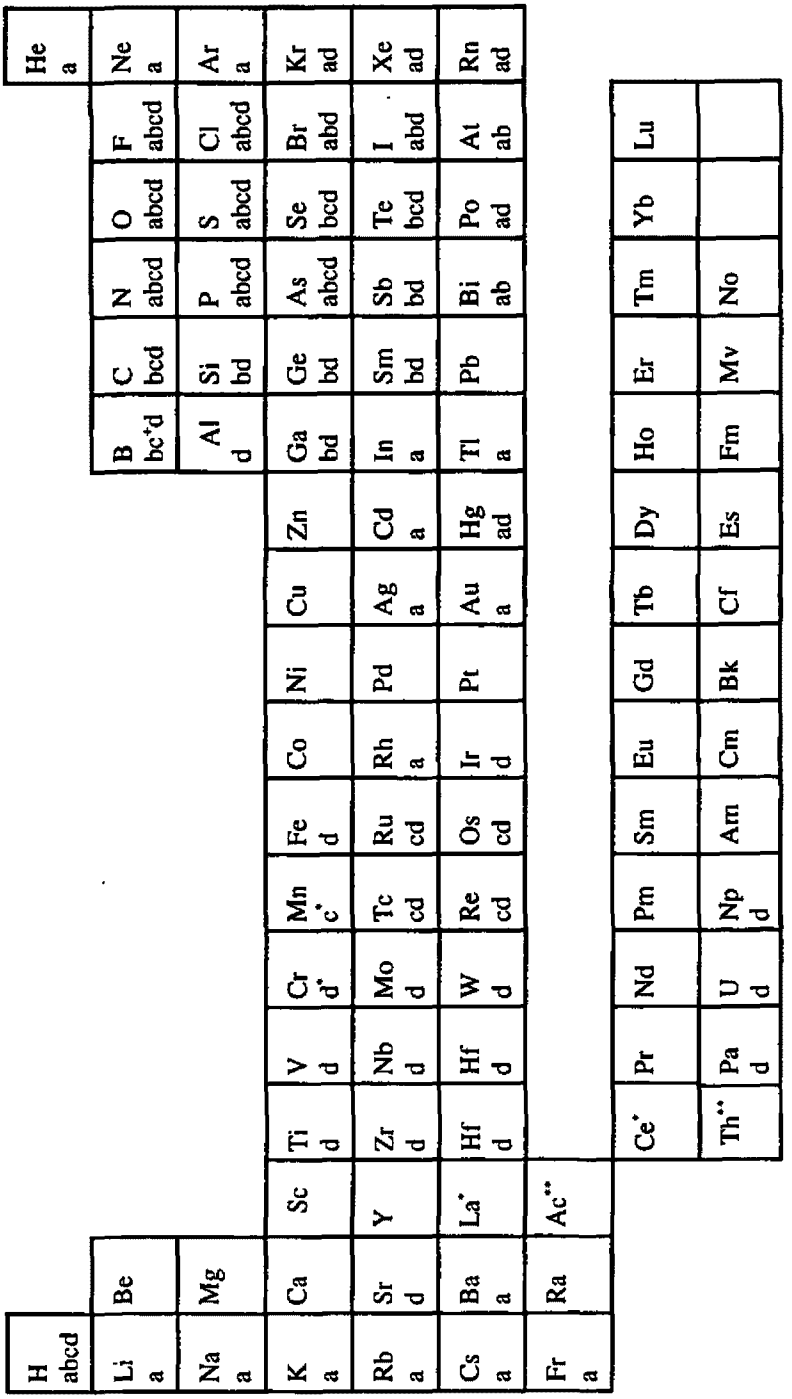
McMillan continues (1975, p. 306):

> "While many of the volatile species are commonly encountered and a large proportion can be produced from aqueous solutions, a significant number are rarely met. The volatilization of highly reactive materials and those with high boiling points are only used in special circumstances, e.g., for very rapid separations. ... Many other volatile compounds have been used to separate the elements, including sulphides, carbonyls, stable organic complexes ... , and fluorinated β-diketones for the lanthanides."

> "Separation, ... , is achieved by differentiation during the volatilization process, fractionation by transfer, and selective collection. Gaseous evolution can be controlled by making use of differences in vapor pressure with temperature, adjustment of the oxidation state of the element in solution or by alteration of the matrix, in order to change the chemical combination of the element. Once gaseous, additional separation is possible and physical processes can be adopted such as gas chromatography, zone refining, fractional distillation, electrostatic precipitation, filtration of condensed phases and low temperature trapping. Chemical methods used are mainly based on the selective trapping of interfering substances by solid or liquid reagents. The methods of preferential collection of the species sought are similar to those used in the transfer stage."Both solid and liquid samples can be used in volatilization separations (Krivan, 1986, p. 377):

> "With solid samples, there are several types of separation methods. The most important of them are ones in which (1) the gas forms a volatile compound with only the trace elements and not the matrix, (2) the gas forms a volatile compound with the matrix but not the trace elements, and (3) volatile compounds are formed with both the matrix and the trace elements. Different gases have been used in separation by volatilization, including inert gases N_2, He, and Ar and the reactive gases H_2O, O_2, H_2, ... F_2, and HF. The apparatus usually consists of

TABLE 14.7 — Elements separable by volatilization as certain species



H abcd																		He a
Li a	Be											B bc*d	C bcd	N abcd	O abcd	F abcd		Ne a
Na a	Mg											Al d	Si bd	P abcd	S abcd	Cl abcd		Ar a
K a	Ca	Sc	Ti d	V d	Cr d*	Mn c*	Fe d	Co	Ni	Cu	Zn	Ga bd	Ge bd	As abcd	Se bcd	Br abd		Kr ad
Rb a	Sr d	Y	Zr d	Nb d	Mo d	Tc cd	Ru cd	Rh a	Pd	Ag a	Cd a	In a	Sm bd	Sb bd	Te bcd	I abd		Xe ad
Cs a	Ba a	La*	Hf d	Hf d	W d	Re cd	Os cd	Ir d	Pt	Au a	Hg ad	Tl a	Pb	Bi ab	Po ad	At ab		Rn ad
Fr a	Ra	Ac**																
			Ce*	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu		
			Th**	Pa d	U d	Np d	Am	Cm	Bk	Cf	Es	Fm	Mv	No				

Key to volatile form of element: a - Element; b - Hydride; c - Oxide; c* - Permanganic acid; d* - Chromyl chloride; d - Halides; d* - Boric acid

(From Coomber, 1975, p307)

three parts: gas regulation and purification, oven with temperature programming and control, and condensation or adsorption with temperature regulation."

"The radiotracer technique provides the best way to determine the recoveries of trace elements in the volatilization process and to optimize the separation with respect to the pertinent experimental parameters."

14.5.3 Distillation Principles

Distillation is the separation of a volatile component(s) of a mixture by vaporization at the boiling point of the mixture and subsequent condensation of the vapor. The vapor produced on boiling the mixture is richer in the more volatile component—the component with the higher vapor pressure (partial pressure) and correspondingly lower boiling point. The process of distillation, therefore, essentially takes advantage of the differences in the boiling points of the constituents to separate a mixture into its components. It is a useful separation tool if the analyte is volatile or can be transformed into a volatile compound. Most inorganic applications of distillation involve batch distillation, whereas most organic applications require some type of fractional distillation. In a simple batch distillation, the sample solution containing a single volatile component or components with widely separated boiling points is placed in a distillation flask, boiling is initiated, and the vapors are then continuously removed, condensed, and collected. Mixtures containing multiple volatile components require *fractional distillation*, which employs repeated vaporization-condensation cycles for separation, and is commonly performed in a *fractionation column* for that purpose. The column allows the cycles to occur in one operation, and the separated component is collected after the last condensation.

Distillation has been widely used for separating organic mixtures but this approach has less applicability in inorganic analysis (Korkisch, 1969, p. 25). Korkisch states: "Nevertheless, some of the elements of interest to radiochemists can be very effectively separated by distillation as their volatile chlorides, bromides, and oxides .... these elements are germanium (Ge), selenium (Se), technetium (Tc), rhenium (Re), ruthenium (Ru), and osmium (Os) (Korkisch, 1969, p. 25; also see DOE, 1995 Method RP530). Two common analytes determined through distillation, tritium and ^{226}Ra, by radon emanation are discussed below.

Specific distillation principles are commonly found in chemistry reference and textbooks. For a theoretical discussion of distillation see Peters (1974) and Perry and Weisberger (1965, pp. 1-229). Distillation procedures are discussed for many inorganic applications in Dean (1995) and for less common radioanalytes in the NAS-NS 3108 Monograph, *Application of Distillation*

Techniques to Radiochemical Separation (DeVoe, 1962), and in NAS-NS 3104 Monograph, *Rapid Radiochemical Separations* (Kuska and Meinke, 1961).

14.5.4 Separations in Radiochemical Analysis

The best known use of distillation in radiochemical analysis is in the determination of tritium (EPA, 1984, pp. H-01-1-8; DOE, 1995, pp. RP580). Water is the carrier as simple distillation is used to separate tritium from water or soil samples. For determination of tritium, the aqueous sample is treated with a small amount of sodium hydroxide (NaOH) and potassium permanganate ($KMnO_4$), and it is then distilled. The early distillate is discarded, and a portion of the distillate is collected for tritium determination by liquid scintillation counting. The alkaline treatment prevents other radionuclides, such as radioiodine or radiocarbon, from distilling over with the tritium (^3H), and the permanganate (MnO_4^{-1}) treatment destroys trace organic material in the sample that could cause quenching during the counting procedure.

Larger samples are distilled using a round-bottom flask, while a MICRO DIST® tube can be utilized for smaller samples (DOE, 1995, Method RP580). The distillate can be added directly to a liquid scintillation cocktail (EPA, 1980, Method 906.0), or further enriched by acid electrolysis (DOE, 1990 and 1997, Method ^{3}H-01) or alkaline electrolysis (DOE, 1990 and 1997, Method ^{3}H-02).

Iodine (I_2) is separated from aqueous samples by distillation from acidic solutions into alkaline solutions (EPA, 1973, pp. 73-76). Iodide (I^{-1}) is added as carrier; but nitric acid (HNO_3) as part of the acid solution, oxidizes the anion to molecular iodine as the mixture is heated for distillation.

One determination of ^{79}Se employs an optional purification step, distillation of the metal as selenous acid, H_2SeO_3 (DOE, 1995, Method RP530). The solution is maintained with excess bromine (Br_2) and hydrobromic acid (HBr) to hold the selenium in the oxyacid form during the distillation. Technetium can be separated from other elements, or can be separated from ruthenium, osmium, or rhenium by distillation of their oxides (Friedlander et al., 1981, p 300). Metals are sometimes distilled in their elemental form—polonium in bismuth or lead (McMillan, 1975, p. 308).

^{226}Ra in solution can be determined by de-emanating its gaseous progeny ^{222}Rn into an ionization chamber or scintillation cell. Generally, the procedure initially involves the concentration of radium by coprecipitation with barium sulfate ($BaSO_4$). The barium sulfate is then dissolved in an EDTA solution, transferred to a sealed bubbler, and stored to allow for the ingrowth of ^{222}Rn. Following sufficient in-growth, the ^{222}Rn is de-emanated by purging the solution with an inert

gas, such as helium (He) or argon (Ar), and is transferred via a drying tube to a scintillation cell or ionization chamber. After the short-lived ^{222}Rn progeny have reached secular equilibrium with the ^{222}Rn (approximately four hours), the sample is counted to determine alpha activity (EPA, 1980, Method 903.1; DOE, 1990 and 1997, Methods Ra-01 through Ra-07; Sedlet, 1966; Lucas, 1990).

When processing samples containing radon, care should be taken to guard against the inadvertent loss of the gas or contamination of the distillation apparatus. Radon can be adsorbed on, or permeate through, materials used in its handling. Diffusion through rubber and plastic tubing or through polyethylene bottles has been observed. Since radon is soluble in many organic compounds, impurities, including greases used in ground-glass connections, can increase adsorption.

14.5.5 Advantages and Disadvantages of Volatilization

14.5.5.1 Advantages

- Can be very selective, producing clean separations.
- Very rapid, especially with high-vacuum equipment.
- Can be performed from solid or liquid samples.
- Most can be performed without a specific carrier gas.

14.5.5.2 Disadvantages

- Relatively few volatile elements or inorganic compounds are available.
- Atmosphere can alter the nature of a volatile form of the tracer or surface material.
- Effects of experimental parameters (carrier gas, gas flow, temperature, time, and recovery) are highly variable.
- Precautions are sometimes necessary to avoid loss of volatile radionuclide substances during subsequent procedures.
- Some systems require high-temperature, complex equipment.
- Contamination of distillate by carrier, spray, or mechanical entrapment is a potential problem.

14.6 Electrodeposition

14.6.1 Electrodeposition Principles

Radionuclides in solution as ions can be deposited (plated) by electrochemical reactions (redox reactions) onto an electrode, either by a spontaneous process (produced by a favorable electrode potential existing between the ion and electrode) or by a nonspontaneous process (requiring the application of an external voltage (potential) (Section 14.2, "Oxidation and Reduction Processes").

Spontaneous electrochemical processes are described by the Nernst equation, which relates the electrode potential of the reaction to the activity of substances participating in a reaction:

$$E=E^0 - RT/nF \ln(a_p/a_r)$$

where E is the electrochemical potential, E^0 is the standard potential for the process, R is the ideal gas constant, T is the absolute temperature, n is the number of electrons exchanged in the redox reaction, F is Faraday's constant, and a_p and a_r are the activities of the products of the reaction and the reactants, respectively. The *activity* (a) of ions in solution is a measure of their molar concentration (c in moles/L) under ideal conditions of infinite dilution. Expressing the activities in terms of the product of molar concentrations and activity coefficients, γ (a measure of the extent the ion deviates from ideal behavior in solution; thus $a=\gamma \cdot c$, where $\gamma \leq 1$), the Nernst equation becomes:

$$E=E^0 - RT/nF \ln(\gamma_p c_p/\gamma_r c_r)$$

For dilute solutions of electrolytes ($\leq 10^{-2}$ molar), the activity coefficient is approximately one ($\gamma \approx 1$; it approaches one as the solution becomes more dilute, becoming one under ideal conditions). Then, the Nernst equation is expressed in terms of the concentrations of ions in solution, the typical form in which the equation is found in most chemistry textbooks (see also Section 14.8.3.1, "Solubility and Solubility Product Constant, K_{sp}," for an application of activity to the solubility product constant):

$$E=E^0 - RT/nF \ln(c_p/c_r)$$

At concentrations less than 10^{-6}M, electrodeposition may show considerable deviations from behavior of macroamounts of elements whose behavior partly depends on the nature and previous treatment of the electrode (Adolff and Guillaumont, 1993, p. 275). Inconsistent

behavior is the result of heterogeneity of the surface metal, a very important consideration when electrodepositing radionuclides at very low concentrations. The spontaneity predicted by the Nernst equation for macroconcentrations of ions in solution at controlled potential is not always observed for microconcentrations (Choppin et al., 1995, p. 246). The activity of radionuclide ions is usually unknown at low concentrations even if the concentration is known, because the activity coefficient (γ) is dependent on the behavior of the mixed electrolytic system. In addition, the concentration might not be accurately known because ions might adsorb on various surfaces, form complexes with impurities, or precipitate on the electrode, for example. (See ection 14.9.3.7, "Oxidation and Reduction of Tracers," for another application of the Nernst equation.) Separation is limited partly because electrodeposition from very dilute solutions is slow, but it is also limited because it rarely leads to complete separation of one element from many others (Coomber, 1975, p. 313). Overall, the behavior of an element during an electrochemical process is determined by its electrochemical potential, which depends on the nature of the ion; its chemical form, its concentration, the general composition of the electrolyte, the current density, material and design of the electrode, and construction features of the electrochemical cell (Zolotov, 1990, pp. 94-95).

Often trace elements are deposited on a solid cathode, but large separation factors between micro- and macro-components are required. This condition is met when electrochemically active metals are the main components or when the analyzed matrix does not contain macro-components that will separate on the cathode (Zolotov, 1990, p. 95). Deposition of heavy metals and actinides can be more difficult to control, for example, because of the decomposition of water and reactions of cations and anions at electrodes (Adolff and Guillaumont, 1993, p. 158). In some cases, deposition of matrix components can be avoided by selection of a suitable medium and composition of the electrolyte. Overall, the effectiveness of electrodeposition of trace components depends on the electrode potential, electrode material and its working surface area, duration of electrolysis, properties of the electrolyte (composition and viscosity), temperature, and mixing rate (Zolotov, 1990, pp. 95-96). Even so, published data are empirical for the most part, and conditions for qualitative reproducible separation are determined for each case. It is difficult, therefore, to make general recommendations for selecting concentration conditions. It is advisable to estimate and account for possible effects of different electrolysis factors when developing separation or concentration methodologies (Zolotov, 1990, p. 98).

14.6.2 Separation of Radionuclides

Although electrodeposition is not frequently used as a radiochemical separation technique, several radionuclides [including iron (Fe) (Hahn, 1945), cadmium (Cd) (Wright, 1947), and technetium (Tc) (Flagg, 1945)] have been isolated by electrodeposition on a metal electrode.

Electrodeposition is, however, the standard separation technique for polonium (Po), copper (Cu), and platinum (Pt). Polonium is isolated through deposition on nickel from a strong hydrochloric acid (HCl) medium (DOE, 1990 and 1997, Method Po-01). This separation is very specific, and, therefore, can be accomplished in the presence of many other radionuclides. Electrodeposition at a mercury cathode has also been used to separate technetium from fission products and for group separation of fission products (Coomber, 1975, p. 198). Numerous metals have been deposited on thin metal films by electrolysis with a magnesium (Mg) cathode. According to Coomber, "Electrodeposition of metals can be sensitive to the presence of other substances" (Coomber, 1975, p. 198). Deposition of polonium on silver (Ag) is inhibited by iron unless a reducing agent is present; and the presence of fluoride (F^{-1}), trace amounts of rare earths, can inhibit the deposition of americium (Am). "In many cases the uncertainties of yield can be corrected by the use of another radioisotope as an internal standard" (Coomber, 1975, p. 198).

14.6.3 Preparation of Counting Sources

Electrodeposition is primarily used to prepare counting sources by depositing materials uniformly in an extremely thin layer. Because of potential self-absorption effects, this approach is ideal for the preparation of alpha sources. Numerous methods have been published for the electrodeposition of the heavy metals, e.g., the Mitchell method from hydrochloric acid (Mitchell, 1960), the Talvitie method from dilute ammonium sulfate [$(NH_4)_2SO_4$] (Talvitie, 1972), and the Kressin method from sodium sulfate-sodium bisulfate media (Kressin, 1977).

Sill and Williams (1981) and Hindman (1983, 1986) contend that coprecipitation is the preferred method for preparation of sources for alpha spectrometry and that the it should be assessed when electrodeposition is being considered. Also see Section 16.7.2, "Coprecipitation," in this manual.

14.6.4 Advantages and Disadvantages of Electrodeposition

14.6.4.1 Advantages

- Highly selective in some cases.
- Deposits material in an extremely thin uniform layer resulting in excellent spectral resolution.
- One of the common methods for preparing actinides for alpha spectrometry.

14.6.4.2 Disadvantages

- Not applicable to many radionuclides.

- Sensitive to the presence of other substances.

- For tracer-level quantities, the process is relatively slow, it seldom leads to complete separation of one element from many others, and there is usually no direct comparison of concentration in solution to deposited activity.

- No further separations can be performed (see Section 16.7.2, "Coprecipitation," for methods using NdF_3.).

14.7 Chromatography

14.7.1 Chromatographic Principles

Chromatography is a separation technique that is based on the unequal distribution (partition) of substances between two immiscible phases, one moving past the other. A mixture of the substances (the analytical mixture) in the *mobile* phase passes over the *immobile phase*. Either phase can be a solid, liquid, or gas, but the alternate phase cannot be in the same physical state. The two most common phase pairs are liquid/solid and gas/liquid. Separation occurs as the components in the mixture partition between the two phases because, in a properly designed chromatographic system, the phases are chosen so that the distribution of the components between the phases is not equal.

With the broad range of choices of phase materials, the number of techniques employed to establish differential distributions of components between the phases, and the various practical laboratory methods used to cause the mobile phases to pass over the immobile phases, there are many chromatographic techniques available in separation chemistry. The names of the chromatographic techniques themselves partially identify the methods or principles employed and suggest the variety of applications available using this approach to separation. They include paper chromatography, ion-exchange chromatography, adsorption chromatography, gas chromatography, high-pressure liquid chromatography, and affinity chromatography. Each aspect of chromatography used in separation chemistry will be described below, including the phases commonly employed, the principles used to establish differential distributions, and the laboratory techniques employed to run a chromatographic separation.

The most common phase pairs used in chromatography are a mobile liquid phase in contact with a solid phase. The liquid phase can be a pure liquid, such as water or an organic solvent, or it can be a solution, such as methyl alcohol, sodium chloride in water, or hexane in toluene. The solid phase can be a continuous material such as paper, or a fine-grained solid such as silica, powdered

charcoal, or alumina. The fine-grained solid can also be applied to a supporting material, such as paper, plastic, or glass, to form a coat of continuous material. Alternatively, gas/liquid phase systems can consist of an inert gas, such as nitrogen (N_2) or helium (He), in conjunction with a high-boiling point liquid polymer coated on the surface of a fine-grained inert material, such as firebrick. This system is called *gas-liquid phase chromatography* (*GLPC*), or simply *gas chromatography* (*GC*). In each system, both phases play a role in the separation by offering a physical or chemical characteristic that will result in differential distribution of the components of the analytical mixture being separated. Liquid/liquid phase systems are similar to gas/liquid phase systems in that one of the liquid phases is bound to an inert surface and remains stationary. These systems are often referred to as *liquid partition chromatography* or *liquid-phase chromatography* (*LPC*), because they are essentially liquid-liquid extraction systems with one mobile and one immobile phase (Section 14.4, "Solvent Extraction").

Differential distributions are established between the separating phases by the combination of physical and chemical properties of the two phases in combination with those of the components of the analytical mixture. The properties that are most commonly exploited by separation chromatography are solubility, adsorption, ionic interactions, complementary interactions, and selective inclusion. One or more of these properties is acting to cause the separation to occur.

14.7.2 Gas-Liquid and Liquid-Liquid Phase Chromatography

In gas-liquid phase chromatography, the components of the analytical mixture are first converted to a vapor themselves and added to the flowing gas phase. They are then partitioned between the *carrier gas* and liquid phases primarily by solubility differences of the components in the liquid phase. As the gas/vapor mixture travels over the liquid phase, the more soluble components of the mixture spend more time in the liquid. They travel more slowly through the chromatography system and are separated from the less soluble, and therefore faster moving, components. Liquid/liquid phase chromatography provides separation based on the same principle of solubility in the two liquid phases, but the separation is performed at ambient temperatures with the components of the analytical mixture initially dissolved in the mobile phase. Partitioning occurs between the two phases as the mobile phase passes over the stationary liquid phase.

Gas chromatography has been used to concentrate tritium, and to separate krypton and xenon fission products and fission-produced halogens (Coomber, 1975, p. 189). A large number of volatile metal compounds could be separated by gas chromatography, but few have been prepared. Lanthanides and trivalent actinides have been separated on glass capillary columns using volatile double halides formed with aluminum chloride (Coomber, 1975, p. 189).

14.7.3 Adsorption Chromatography

Adsorption chromatography partitions components of a mixture by means of their different adsorption characteristics onto the surface of a solid phase and their different solubilities in a liquid phase. Adsorption phenomena are primarily based on intermolecular interactions between the chemical components on the surface of the solid and the individual components of the mixture. They include Van der Waals forces, dipole-dipole interactions, and hydrogen bonds. Silica is a useful adsorption medium because of the ability of its silyl OH groups to hydrogen bond or form dipole-dipole interactions with molecules in the mixture. These forces compete with similar intermolecular interactions—between the liquid phase and the components of the mixture—to produce the differential distribution of the components. This process causes separation to occur as the liquid phase passes over the solid phase.

Many separations have been performed via paper and thin-layer chromatography. Modified and treated papers have been used to separate the various valence states of technetium (Coomber, 1975, p. 189).

14.7.4 Ion-Exchange Chromatography

14.7.4.1 Principles of Ion Exchange

Since the discovery by Adams and Holmes (1935) that synthetic resins can have ion-exchanging properties, ion exchange has become one of the most popular, predominant, and useful techniques for radiochemical separations, both with and without carriers. There are many excellent references available in the literature, e.g., Dean (1995), Dorfner (1972), Korkisch (1989), Rieman and Walton (1970), and NAS monographs (listed in References, under the author's name). The journal, *Ion Exchange and Solvent Extraction,* reports recent advances in this field of separation.

Ion-exchange methods are based on the reversible exchange of metal ions between a liquid phase, typically water, and a solid ionic phase of opposite charge, the *resin.* The resin competes with the ion-solvent interactions in the liquid phase, primarily ion-dipole interactions and hydrogen bonding, to produce the selective partition of ions, causing separation. The solid phase consists of an insoluble, but permeable, inert polymeric *matrix* that contains fixed charged groups (exchange sites) associated with mobile counter-ions of opposite charge. It is these counter-ions that are exchanged for other ions in the liquid phase. Resins are either naturally occurring substances, such as zeolites (inorganic silicate polymers) or synthetic polymers. The synthetic resins are organic polymers with groups containing the exchange sites. The *exchange sites* are acid or base groups (amines, phenols, and carboxylic or sulfonic acids) used over a specific pH range

where they are in their ionic form. Typical exchange groups for cations (K^{+1}, Ca^{+2}, and UO_2^{+2}) are the sulfonate anion, RSO_3^{-1}, or the carboxylate anion, $RCOO^{-1}$. The quaternary-amine cation, RNH_3^{+1}, or its derivative, is a common exchange group for anions (Cl^{-1}, OH^{-1}, and $UO_2(SO_4)_3^{-4}$).

In a practical description of ion-exchange equilibria, the *weight distribution coefficient, K_d*, and the *separation factor*, α, are significant. The weight distribution coefficient is defined as:

$$K_d = (C_1/g_{resin}) / (C_2 /mL_{solution})$$

where C_1 is the weight of metal ion adsorbed on 1 g of the dry resin, and C_2 is the weight of metal that remains in 1 mL of solution after equilibrium has been reached. The separation factor refers to the ratio of the distribution coefficients for two ions that were determined under identical experimental conditions:

$$\text{Separation factor } (\alpha) = K_{d,a} / K_{d,b}$$

where *a* and *b* refer to a pair of ions. This ratio determines the separability of the two ions; separation will only be achieved if $\alpha \neq 1$. The more that α deviates from unity, the easier it will be to obtain separation.

An example of the separation process is the cation-exchange resin. It is usually prepared for separation procedures as a hydrogen salt of the exchange group. Separation occurs when an aqueous solution of another alkali-metal ion (i.e., Li^{+1}, K^{+1}, Rb^{+1}, or Cs^{+1}) comes in contact with the resin. Different ions bond selectively to the exchange group, depending on the separation conditions, displacing the counter-ion that is present in the prepared resin as follows:

$$R_{esin}SO_3^{-1}H^{+1} + Cs^{+1} - R_{esin}SO_3^{-1}Cs^{+1} + H^{+1}$$

Diffusion is an important process during ion exchange; the solute ions must penetrate the pores of the spherical resin beads to exchange with the existing ions. Equilibrium is established between each ion in the analyte solution and the exchange site on the resin. The ion least tightly bonded to the exchange site and most solvated in solution spends more time in solution. Selective bonding is a factor of the size and charge of the ion, the nature of the exchange group, and the pH and ionic strength of the media. The order of strength of bonding at low acid concentrations in this example is H^{+1} or $Li^{+1} < Na^{+1} < K^{+1} < Rb^{+1} < Cs^{+1}$ (Showsmith, 1984). Under the appropriate conditions, for example, Cs^{+1} will bond exclusively, or Cs^{+1} and Rb^{+1} will bond, leaving the remaining cations in solution. The process can be operated as a batch operation or via continuous-flow with the resin in an ion-exchange column. In either case, actual separation is

achieved as the equilibrated solution elutes from the resin, leaving select ions bonded to the resin and others in solution. The ion that spends more time in solution elutes first. The ability to "hold" ionic material is the resin capacity, measured in units of mg or meq per gram of resin. Eventually, most of the exchange groups are occupied by select ions. The resin is essentially saturated, and additional cations cannot bond. In a continuous-flow process, *breakthrough* will then occur. At this time, added quantities of select cations (Cs^{+1} or Cs^{+1} and Rb^{+1} in this example) will pass through the ion-exchange column and appear in the output solution (*eluate*). No further separation can occur after breakthrough, and the bonded ions must be remove to prepare the column for additional separation. The number of bed volumes of incoming solution (*eluant*) that passes through a column resin before breakthrough occurs provides one relative measure of the treatment capacity of the resin under the conditions of column use. The bonded cations are displaced by adjusting the pH of the medium to change the net charge on the exchange groups. This change alters the ability of the exchange groups to attract ions, thereby replacing the bonded cations with cations that bond more strongly. More commonly, the resin is treated with a more concentrated solution of the counter-ion—H^{+1} in this example. Excess H^{+1} favors the equilibrium that produces the initial counter-ion form of the exchange group. This process that returns the column to its original form is referred to as "regeneration."

Overall, selectivity of the exchange resin determines the efficiency of adsorption of the analyte from solution, the ease with which the ions can be subsequently removed from the resin, and the degree to which two different ions of like charge can be separated from each other. The equilibrium distribution of ions between the resin and solution depends on many factors, of which the most important are the nature of the exchanging ions, the resin, and the solution:

- In dilute solutions, the stationary phase will show preference for ions of higher charge.
- The selectivity of ion exchangers for ions increases with the increase of atomic number within the same periodic group, i.e., $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$.
- The higher the polarizability and the lower the degree of solvation (favored by low charge and large size), the more strongly an ion will be adsorbed.
- Resins containing weakly acidic and weakly basic groups are highly selective towards H^+ and OH^- ions. Ion-exchange resins that contain groups capable of complex formation with particular ions will be more selective towards those ions.
- As cross-linking is increased (see discussion of resins below), resins become more selective in their behavior towards ions of different sizes.

- No variation in the eluent concentration will improve the separation for ions of the same charge; however, for ions of different net charges, the separation does depend on the eluent concentration.

14.7.4.2 Resins

The most popular ion-exchange resins are polystyrenes cross-linked through divinylbenzene (DVB). The percentage of DVB present during polymerization controls the extent of cross-linking. Manufacturers indicate the degree of cross-linking by a number following an X, which indicates the percentage of DVB used. For instance, AG 1-X8 and AG 1-X2 are 8 percent and 2 percent cross-linked resins, respectively. As this percentage is increased, the ionic groups effectively come into closer proximity, resulting in increased selectivity. However, increases in cross-linking decrease the diffusion rate in the resin particle. Because diffusion is the rate-controlling step in column operations, intermediate cross-linking in the range of 4 to 8 percent is commonly used.

Particle diameters of 0.04-0.3 mm (50-400 mesh) are commonly used, but larger particles give higher flow rates. Difficult separations can require 200-400 mesh resins. Decreasing the particle size reduces the time required for attaining equilibrium; but at the same time, it decreases flow rate. When extremely small particle sizes are used, pressure must be applied to the system to obtain acceptable flow rates (see discussion of high pressure liquid chromatography in Section 14.7.7, "Chromatographic Methods").

Ion-exchange resins are used in batch operations, or more commonly, in column processes in the laboratory. Columns can be made in any size desired. The diameter of the column depends on the amount of material to be processed, and the length of the column depends primarily on the difficulty of separations to be accomplished. Generally, the ratio of column height to diameter should be 8:1. Higher ratios lead to reduced flow rate; lower ratios might not provide effective separations.

Some other factors should be considered when using ion-exchange resins:

- Resins should not be allowed to dry out, especially during analysis. Rehydration of dried resins will result in cracking; these resins should not be used.

- Non-ionic and weakly ionic solutes may be absorbed (not exchanged) by the resin. These materials, if present during analysis, can alter the exchange characteristics of the resin for certain ions.

- Particulate matter present in the analyte solution may be filtered by the resin. This material will have several undesired effects, such as decreased flow rate, reduced capacity, and ineffective separation.

- Organic solvents suspended in the analyte solution from previous separation steps can be adsorbed by the resin creating separation problems.

Ion exchangers are classified as *cationic* or *anionic* (*cation exchangers* or *anion exchangers*, respectively), according to their affinity for negative or positive counter-ions. They are further subdivided into strongly or weakly ionized groups. Most cation exchangers (such as Dowex-50 and Amberlite IR-100) contain free sulfonic acid groups, whereas typical anion exchangers (such as AG 1 and Dowex-1) have quaternary amine groups with replaceable hydroxyl ions (see Table 14.8).

TABLE 14.8 — Typical functional groups of ion-exchange resins

Cation Exchangers	Anion Exchangers
$-SO_3H$	$-NH_2$
-COOH	-NHR
-OH	$-NR_2$
-SH	$-NR_3^+$

R=alkyl group

The sulfonate resins are known as *strong acid cation (SAC) resins* because the anion is derived from a strong sulfonic acid (RSO_3H). Likewise, the carboxylate resins are known as *weak acid cation (WAC) resins* because the anion is derived from a weak carboxylic acid (RCOOH). R in the formulas represents the inert matrix. The quaternary-amine cation (RNH_3^{+1}) or its derivatives, represents the common exchange group for anions.

Several examples from the literature illustrate the use of ion-exchange chromatography for the separation of radionuclides. Radium is separated from other alkaline-earth cations (Be^{+2}, Mg^{+2}, Ca^{+2}, Sr^{+2}, and Ba^{+2}) in hydrochloric solutions on sulfonated polystyrene resins (Kirby and Salutsky, 1964, pp. 26-27), or converted to an anionic complex with citrate or EDTA and separated on a quaternary ammonium polystyrene resin (Sedlet, 1966, p. 302).

Anion-exchange resins separate anions by an analogous process beginning with a prepared resin, usually in the chloride form ($RNH_3^{+1}Cl^{-1}$), and adding a solution of ions. Anion-exchange

chromatography is used in one step of a procedure to isolate thorium for radioanalysis by alpha counting (EPA, 1984, pp. U/Th-01-1-14). Thorium cations (Th^{+4}) form anionic nitrate complexes that bind to an anion-exchange resin containing the quaternary complex, $R\text{-}CH_2\text{-}N(CH_3)_3^{+1}$. Most metal ion impurities do not form the complex and, as cations, they do not bind to the exchanger, but remain with the liquid phase. Once the impurities are removed, thorium itself is separated from the resin by treatment with hydrochloric acid (HCl) that destroys the nitrate complex, leaving thorium in its +4 state, which will not bind to the anionic exchanger.

A selection of commercially available resins commonly employed in the radiochemistry laboratory is given in Table 14.9.

The behavior of the elements on anion- and cation-exchange resins is effectively summarized for several resins in Faris and Buchanan (Faris and Buchanan, 1964), Kraus and Nelson (Kraus and Nelson, 1956), and Nelson et al. (1964). The behavior in concentrated hydrochloric acid is illustrated for cations on cation-exchange resins in Figure 14.3 (Dorfner, 1972, p. 208) and for cations on anion-exchange resins in Figure 14.4 (Dorfner, 1972, p. 210).

TABLE 14.9 — Common ion-exchange resins [1]

Resin type & nominal % cross-link	Minimum wet capacity meq• mL^{-1}	Density (nominal) g• mL^{-1}	Description
Anion-exchange resins — gel type — strongly basic — quaternary ammonium functionality			
Dowex, AG or Eichrom 1- X 4	1.0	0.70	Strongly basic anion exchanger with S-DVB matrix for separation of organic acids, nucleotides, and other anions. Molecular weight exclusion < 1400.
Dowex, AG or Eichrom 1- X 8	1.2	0.75	Strongly basic anion exchanger with S-DVB matrix for separation of inorganic and organic anions with molecular weight exclusion < 1000. 100-200 mesh is standard for analytical separations.
Anion-exchange resins — gel type — intermediate basicity			
Bio-Rex 5	1.1	0.70	Intermediate basic anion exchanger with primary tertiary amines on an polyalkylene-amine matrix for separation of organic acids.
Anion-exchange resins — gel type — weakly basic — polyamine functionality			
Dowex or AG 4- X 4	0.8	0.7	Weakly basic anion exchanger with tertiary amines on an acrylic matrix. Suitable for use with high molecular weight organic compounds.
Amberlite IRA-68	1.6	1.06	Acrylic-DVB with unusually high capacity for large organic molecules.

Resin type & nominal % cross-link	Minimum wet capacity meq• mL^{-1}	Density (nominal) g• mL^{-1}	Description
Cation-exchange resins - gel type - strongly acidic - sulfonic acid functionality			
Dowex, AG or Eichrom 50W- X4	1.1	0.80	Strongly acidic cation exchanger with S-DVB matrix for separation of amino acids, nucleosides and cations. Molecular weight exclusion is < 1400.
Dowex, AG or Eichrom 50W- X8	1.7	0.80	Strongly acidic cation exchanger with S-DVB matrix for separation of amino acids, metal cations, and cations. Molecular weight exclusion is < 1000. 100-200 mesh is standard for analytical applications.
Amberlite IR-120	1.9	1.26	8% styrene-DVB type; high physical stability.
Selective ion-exchange resins			
Duolite GT-73	1.3	1.30	Removal of Ag, Cd, Cu, Hg, and Pb.
Amberlite IRA-743A	0.6	1.05	Boron-specific.
Amberlite IRC-718	1.0	1.14	Removal of transition metals.
Chelex® 100	0.4	0.65	Weakly acidic chelating resin with S-DVB matrix for heavy metal concentration.
Eichrom Diphonix®			Chelating ion-exchange resin containing geminally substituted diphosphonic groups chemically bonded to a styrenic-based polymer matrix. Extraordinarily strong affinity for actinides in the tetra- and hexavalent oxidation states from highly acidic media.
Anion exchanger — macroreticular type — strongly basic — quaternary ammonium functionality			
AG MP-1	1.0	0.70	Strongly basic macroporous anion exchanger with S-DVB matrix for separation of some enzymes, and anions of radionuclides.
Cation-exchange resin — macroreticular type — sulfonic acid functionality			
AG MP-50	1.5	0.80	Strongly acidic macroporous cation exchanger with S-DVB matrix for separation of cations of radionuclides and other applications.
Microcrystalline exchanger			
AMP-1	4.0		Microcrystalline ammonium molybophosphate with cation exchange capacity of 1.2 meq/g. Selectively adsorbs larger alkali-metal ions from smaller alkali-metal ions, particularly cesium.

(1) Dowex is the trade name for Dow resins; AG and Bio-Rex are the trade names for Bio-Rad Laboratories resins; Amberlite is the trade name of Rohm & Haas resins. MP is the acronym for macroporous resin; S-DVB is the acronym for styrene-divinylbenzene.

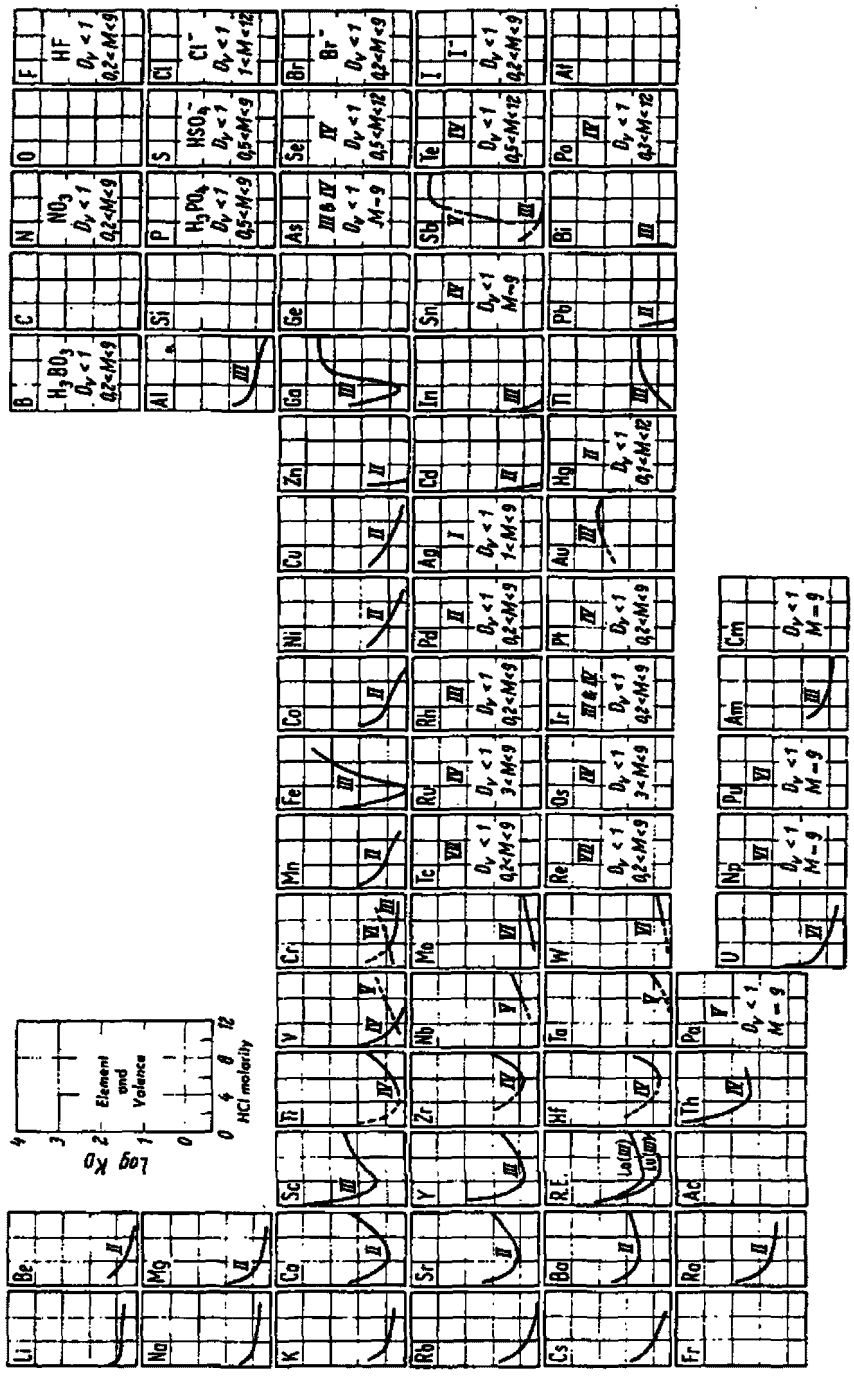


FIGURE 14.3 — The behavior of elements in concentrated hydrochloric acid on cation-exchange resins

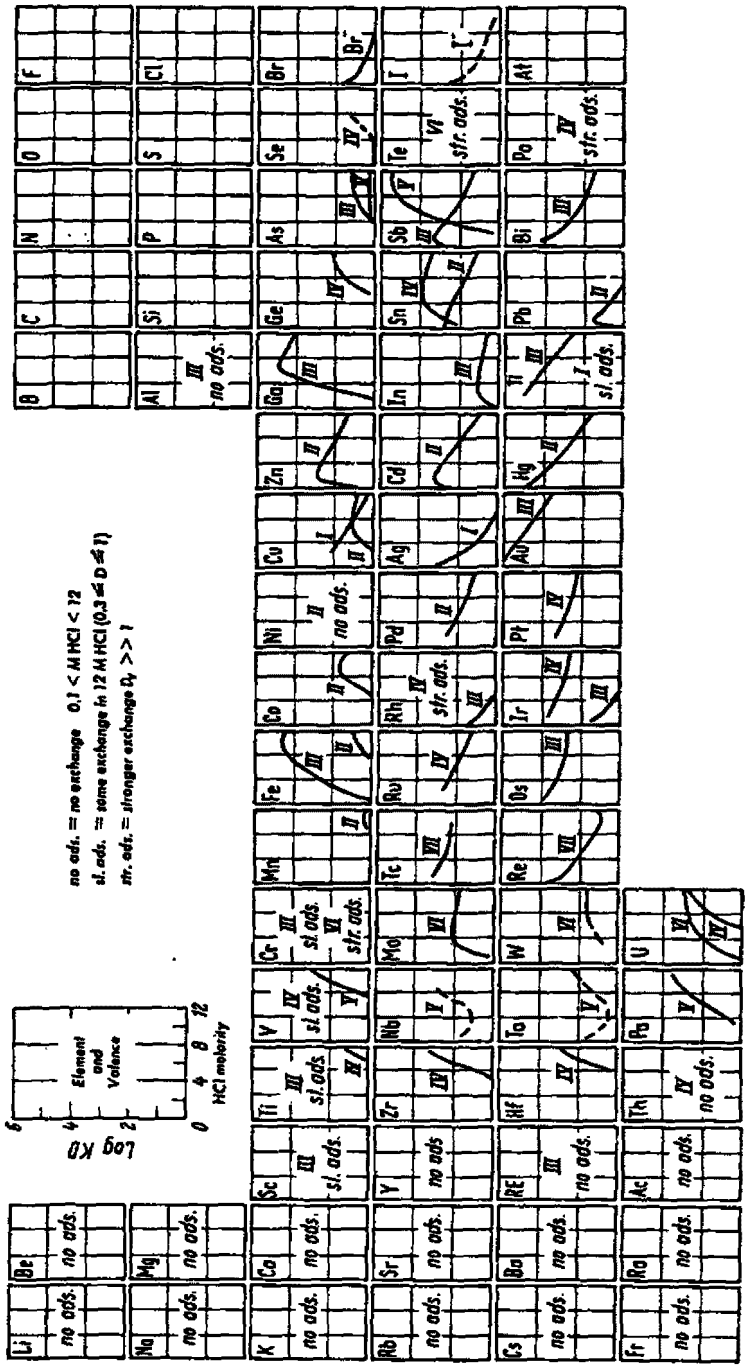


Figure 14.4 —The behavior of elements in concentrated Hydrochloric acid on anion-exchange resins

14.7.5 Affinity Chromatography

Several newer types of chromatography are based on highly selective and specific attractive forces that exist between groups chemically bound to an inert solid matrix (ligands) and molecular or ionic components of the analytical mixture. Affinity chromatography is an example of this separation technique, which is used in biochemistry to isolate antigenic materials, such as proteins. The proteins are attracted to their specific antibody that is bonded to a solid matrix. These attractive forces are often called complementary interactions because they are based on a lock-and-key type of fit between the two constituents. The interaction is complementary because the two components match (fit) each other in size and electrical nature.

Crown ethers bonded to solid matrices serve as ligands in a chromatographic separation of radium ions from aqueous solutions containing other cations (see Section 14.4.5.1, "Extraction Chromatography Columns"). Even other alkaline-earth cations with the same +2 charge, such as strontium (Sr^{+2}) and barium (Ba^{+2}), offer little interference with radium binding because the cyclic nature of the crown ether creates a ring structure with a cavity that complements the radius of the radium ion in solution. In addition, the oxygen atoms of the cyclic ether are inside the ring, allowing these electron-dense atoms to form effective ion-dipole interactions through water molecules with the radium cation. Radionuclides analyzed by this method include $^{89}Sr/^{90}Sr$, ^{99}Tc, ^{90}Y, and ^{210}Pb.

14.7.6 Gel-Filtration Chromatography

Another physical property that is used to separate molecules by a chromatographic procedure is the effective size (molecular weight) of the molecule. High molecular-weight ions can also be separated by this procedure. The method is known by several names, including *gel-filtration chromatography*, *molecular-sieve filtration*, *exclusion chromatography*, and *gel-permeation chromatography*. This technique is primarily limited to substances such as biomolecules with molecular weights greater than 10,000 Daltons. In similar types of solutions (similar solutes and similar concentrations), the molecules or ions have a similar shape and molecular weight that is approximately proportional to the hydrodynamic diameter (size) of the molecule or ion. The solid phase consists of a small-grain inert resin that contains microscopic pores in its matrix that will allow molecules and ions up to a certain diameter, called *included particles*, to enter the resin. Larger particles are *excluded*. Of the included particles, the smaller ones spend more time in the matrices. Separation of the molecules or ions is based on the fact that those substances that are excluded are separated in a batch from the included substances, while those that are included are separated by size. The log of the molecular weight of the included molecules or ions is approximately inversely proportional to the time the particles spend in the matrix.

14.7.7 Chromatographic Laboratory Methods

Chromatographic separations are achieved using a variety of laboratory techniques. Some are actually quite simple to perform, while others require sophisticated instrumentation. *Paper chromatography* employs a solid-liquid phase system that separates molecules and ions with filter paper or similar material in contact with a developing solvent. The analytical mixture in solution is spotted at the bottom of the paper and allowed to dry, leaving the analytes on the paper. The paper is suspended so that a small part of the bottom section is in a solvent, but not so deep that the dry spots enter the solvent. By capillary action, the solvent travels up the paper. As the solvent front moves up, the chromatogram is produced with the components of the mixture partitioning between the liquid phase and the paper. *Thin-layer chromatography* is similar, but the paper is replaced by a thin solid phase of separatory material (silica gel, alumina, cellulose, etc.) coated on an inert support, such as plastic or glass.

Column chromatography can accommodate a larger quantity of both phases and can, therefore, separate greater quantities of material by accepting larger loads or provide more separating power with an increased quantity of solid phase. In the procedure, a solid phase is packed in a glass or metal column and a liquid phase is passed through the column under pressure supplied by gravity or low-pressure pumping action. For this reason, gravity flow (or pumping the liquid phase under pressures similar to those generated by gravity flow) is often referred to as *low-pressure chromatography*. The liquid phase is usually referred to as the *eluent* and the column is *eluted* with the liquid. Column chromatography is the common method used in ion-exchange chromatography. With column chromatography, separation depends on: (1) type of ion-exchange resin used (i.e., cationic, anionic, strong, or weak); (2) eluting solution (its polarity affects ion solubility, ionic strength affects displacement of separating ions, and pH affects net charge of exchange groups or their degree of ionization in solution); (3) flow rate, grain size, and temperature, which affect how closely equilibrium is approached (generally, low flow rate, small grain size, and high temperature aid the approach to equilibrium and, therefore, increase the degree of separation); and (4) column dimensions (larger diameter increases column capacity, while increased length increases separation efficiency by increasing distance between ion bands as they travel through the column) (Wahl and Bonner, 1951, pp.137-139).

Metal columns can withstand considerably more pressure than glass columns. *High-pressure liquid chromatography* (HPLC) employs stainless steel columns and solid phases designed to withstand high pressures without collapsing. The method is noted for its rapid separation times because of relatively high flow rates under high pressures (up to 2,000 lbs/in^2). For this reason, the acronym HPLC alternatively represents *high-performance liquid chromatography*. HPLC is often performed with a liquid-partition technique between an aqueous phase and organic phase,

but gel filtration, ion exchange, and adsorption methods are also employed. In the case of liquid-partition separations, either a stationary aqueous phase or stationary organic phase is selected. The former system is referred to as normal phase chromatography and the latter as reversed phase chromatography, a holdover from the first applications of the technique that employed a stationary aqueous phase. The aqueous phase is made stationary by adsorption onto a solid support, commonly silica gel, cellulose powder, or polyacrylamide. An organic stationary phase is made from particles of a polymer such as polyvinyl chloride or Teflon®. Reversed phase HPLC has been used to separate individual elements of the lanthanides and actinides and macroquantities of actinides (Choppin et al., 1995, p. 248).

Gas/liquid phase systems are also used. During gas-liquid phase chromatography (GLPC) [or simply, gas chromatography (GC)], the gas phase flows over the liquid phase (coated onto an inert solid) as an inert carrier gas—commonly helium (He) or nitrogen (N_2)—flows through the system at low pressure. The carrier gas is supplied from a tank of the stored gas.

14.7.8 Advantages and Disadvantages of Chromatographic Systems

Ion-exchange chromatography is by far the predominant chromatographic method used for the separation of radionuclides. Its advantages and disadvantages is presented exclusively in this section.

Advantages

- Highly selective.
- Highly efficient as a preconcentration method.
- Works as well with carrier-free tracer quantities as with weighable amounts.
- Produces a high yield (recovery).
- Can separate radionuclides from interfering counter-ions.
- Simple process requiring simple equipment.
- Wide scope of applications.
- Can handle high volumes of sample.

Disadvantages

- May require high volume of eluent.
- Usually a relatively slow process, but rapid selective elution processes are known.
- Requires narrow pH control.

14.8 Precipitation and Coprecipitation

14.8.1 Introduction

Two of the most common and oldest methods for the separation and purification of ions in radioanalytical chemistry are *precipitation* and *coprecipitation*. Precipitation is used to isolate

and collect a specific radionuclide from other (foreign) ions in solution by forming an insoluble compound. Either the radionuclide is precipitated from solution itself, or the foreign ions are precipitated, leaving the radionuclide in solution. Sometimes a radionuclide is present in solution at sub-micro concentrations, i.e., levels so low that the radionuclide will not form an insoluble compound upon addition of a counter-ion. In these cases, the radionuclide can often be brought down from solution by coprecipitation, associating it with an insoluble substance that precipitates from solution. This phenomenon is especially important in gravimetric analysis and radiochemistry. In gravimetric analysis, carrying down of impurities is a problem. For radiochemists, coprecipitation is a valuable tool.

14.8.2 Solutions

Precipitation and coprecipitation provide an analytical method that is applied to ions in solution. *Solutions* are simply homogeneous mixtures (a physical combination of substances), which can be solids, liquids, or gases. The components of a solution consist of a *solute* and a *solvent.* The solute is generally defined as the substance that is dissolved, and the solvent is the substance that dissolves the solute. In an alternative definition, particularly suitable for liquid components when it is not clear what is being dissolved or doing the dissolving, the solute is the minor constituent and the solvent is the major constituent. In any event, the solute and solvent can consist of any combinations of substances, so long as they are soluble in each other. However, in this chapter, we are generally referring to aqueous solutions in which a solute is dissolved in water. The terms below further describe solutions:

- *Solubility* is defined as the concentration of solute in solution that exists in equilibrium with an excess of solute; it represents the maximum amount of solute that can dissolve in a given amount of the solvent. The general solubilities of many of the major compounds of concern are described in Table 14.10.

- An *unsaturated solution* is one in which the concentration of the solute is less than the solubility. When additional solute is added to an unsaturated solution, it dissolves.

- A *saturated solution* is one that is in equilibrium with an excess of the solute. The concentration of a saturated solution is equal to the solubility of the solute. When solute is added to the saturated solution, no more solute dissolves.

- A *supersaturated solution* is a solution in which the concentration of solute is temporarily greater than its solubility—an unstable condition. Therefore, when additional solute is added

to a supersaturated solution, solute comes out of solution as solid until the concentration decreases to that of the saturated solution.

TABLE 14.10 — General solubility behavior of some cations of interest [1]

The Common Cations

Na^{+1}, K^{+1}, NH_4^{+1}, Mg^{+2}, Ca^{+2}, Sr^{+2}, Ba^{+2}, Al^{+3}, Cr^{+3}, Mn^{+2}, Fe^{+2}, Fe^{+3}, Co^{+2}, Ni^{+2}, Cu^{+2}, Zn^{+2}, Ag^{+1}, Cd^{+2}, Sn^{+2}, Hg_2^{+2}, Hg^{+2}, and Pb^{+2}

There are general rules of solubilities for the common cations found in most basic chemistry texts (e.g., Pauling, 1970, p. 453).

Under the class of *mainly soluble substances*:

- All nitrates (NO_3^-) are soluble.
- All acetates ($C_2H_3O_2^-$) are soluble.
- All chlorides (Cl^-), bromides (Br^-), and iodides (I^-) are soluble, except for those of silver, mercury, and lead. $PbCl_2$ and $PbBr_2$ are sparingly soluble in cold water, and more soluble in hot water.
- All sulfates (SO_4^{-2}) are soluble, except those of barium, strontium, and lead. $CaSO_4$, Ag_2SO_4, and Hg_2SO_4 are sparingly soluble.
- Most salts of sodium (Na), potassium (K), and ammonium (NH4+) are soluble. Notable exceptions are $NaSb(OH)_6$, $K_3Co(NO_2)_6$, K_2PtCl_6, $(NH_4)_2PtCL_6$, and $(NH_4)_3Co(NO_2)_6$.

Under the class of *mainly insoluble substances*:

- All hydroxides (OH^{-1}) are insoluble, except those of the alkali metals (Li, Na, K, Rb, and Cs), ammonium, and barium (Ba). $Ca(OH)_2$ and $Sr(OH)_2$ are sparingly soluble.
- All normal carbonates (CO_3^{-2}) and phosphates (PO_4^{-3}) are insoluble, except those of the alkali metals and ammonium. Many hydrogen carbonates and phosphates are soluble, i.e., $Ca(HCO_3)_2$, $Ca(H_2PO_4)_2$.
- All sulfides (S^{-2}), except those of the alkali metals, ammonium, and the alkaline-earth metals (Be, Mg, Ca, Sr, Ba, and Ra), are insoluble. Both aluminum- and chromium sulfide are hydrolyzed by water, resulting in the precipitation of $Al(OH)_3$ and $Cr(OH)_3$.
- Some cations, such as Ba^{+2}, Pb^{+2}, and Ag^{+1}, form insoluble chromates (CrO_4^{-2}), which can be used as a basis for separation.

Actinide Elements

The solubility properties of the actinide M^{+3} ions are similar to those of the tripositive lanthanide ions, while the behavior of the actinide M^{+4} ions closely resembles that of Ce^{+4}.

- The *fluorides (F^-), oxalates ($C_2O_4^{-2}$), hydroxides (OH^-), and phosphates* are insoluble.
- The *nitrates, halides (except fluorides), sulfates, perchlorates (ClO_4^-), and sulfides* are all soluble.

(1) Solubility data for specific compounds can be found in the CRC Handbook of Chemistry and Physics (CRC, 1999) and in the NAS-NS monographs.

14.8.3 Precipitation

Precipitation is accomplished by combining a selected ion(s) in solution with a suitable counter-ion in sufficient concentrations to exceed the solubility of the resulting compound and produce a supersaturated solution. Nucleation occurs and growth of the crystalline substance then proceeds in an orderly manner to produce the precipitate (see Section 14.8.3.1, "Solubility and the Solubility Product Constant, K_{sp}"). The precipitate is collected from the solvent by a physical method, such as filtration or centrifugation. A cation (such as Sr^{+2}, for example) will precipitate from an aqueous solution in the presence of a carbonate anion, forming the insoluble compound, strontium carbonate ($SrCO_3$), when sufficient concentrations of each ion are present in solution to exceed the solubility of $SrCO_3$. The method is used to isolate and collect strontium from water for radioanalysis (EPA, 1984, pp. Sr-04-1-19).

A precipitation process should satisfy three main requirements:

- The targeted species should be precipitated quantitatively.
- The resulting precipitate should be in a form suitable for subsequent handling; it should be easily filterable and should not creep.
- If it is used as part of a quantitative scheme, the precipitate should be pure or of known purity at the time of weighing for gravimetric analysis.

Precipitation processes are useful in several different kinds of laboratory operations, particularly gravimetric yield determinations—as a separation technique and for preconcentration—to eliminate interfering ions, or for coprecipitation.

1719 14.8.3.1 Solubility and the Solubility Product Constant, K_{sp}

1720 Chemists routinely face challenges in the laboratory as a result of the phenomenon of solubility.
1721 Examples include keeping a dissolved component in solution and coprecipitating a trace-level
1722 analyte from solution.

1723 *Solubility equilibrium* refers to the equilibrium that describes a solid dissolving in solution, such
1724 as strontium carbonate dissolving in water, for example:

1725 $$SrCO_3(s) \rightarrow Sr^{+2}(soln) + CO_3^{-2}(soln)$$

1726 or, alternately, a solid forming from solution, with the carbonate precipitating:

1727 $$Sr^{+2}(soln) + CO_3^{-2}(soln) \rightarrow SrCO_3(s)$$

1728 The *solubility product constant*, K_{sp}, is the equilibrium constant for the former process, a solid
1729 dissolving and forming ions in solution. Leussing explains K_{sp} in general terms as follows:

1730 "For an electrolyte, M_mN_n, which dissolves and dissociates according to the equation:

1731 $$M_mN_n(s) \leftrightharpoons M_mN_n(soln) \leftrightharpoons mM^{+n}(soln.) + nN^{-m}(soln.)$$

1732 "The equilibrium conditions exists that:

1733 $$a_{MmNn(s)} = a_{MmNn(soln)} = a^{m}_{M+n(soln)} \cdot a^{n}_{N-m(soln.)}$$

1734 "[The value *a* is the *activity* of the ions in solution, a measure of the molar concentration
1735 (moles/L) of an ion in solution under ideal conditions of infinite dilution.] (Also see Section
1736 14.6.1, *Principles of Electrodeposition*, for a discussion of activity as applied to the Nernst
1737 equation.) [This equation] results in the familiar solubility product expression since the
1738 activity of a solid under given conditions is a constant. Expressing the activities in terms of
1739 the product of molar concentrations and *activity coefficients*, γ [a measure of the extent the
1740 ion deviates from ideal behavior in solution; thus $a = \gamma \cdot c$ where $\gamma \leq 1$], [this] equation
1741 becomes...

1742 $$[M^{+n}]^m [N^{-m}]^n \gamma^{m}_{M+n} \gamma^{n}_{N-m} = \text{a constant} = K_{sp}$$

1743 (Leussing, 1959, pp. 689-690).

For dilute solutions of electrolytes ($\leq 10^{-2}$ molar), the activity coefficient is approximately one ($\gamma \approx 1$; it approaches one as the solution becomes more dilute, becoming one under the ideal conditions of infinite dilution). Then, the solubility product constant is expressed in terms of the concentrations of ions in solution, the typical form in which the equation is found in most chemistry textbooks:

$$K_{sp}=[M^{+n}]^m\,[N^{-m}]^n$$

For strontium carbonate, K_{sp} is defined in terms of the concentrations of Sr^{+2} and CO_3^{-2}:

$$K_{sp} = [Sr^{+2}][CO_3^{-2}] = 1.6 \times 10^{-9}$$

In order for the carbonate to precipitate, the product of the concentration of the ions in solution representing the ions in the equilibrium expression, the *common ions,* must exceed the value of the K_{sp}. The concentration of each common ion does not have to be equal. For example, if $[Sr^{+2}]$ is 1×10^{-6} molar, then the carbonate ion concentration must be greater than 0.0016 molar for precipitation to occur because $(1 \times 10^{-6}) \times (.0016) = 1.6 \times 10^{-9}$.

At higher concentrations ($\geq 10^{-2}$ molar), where the ions in solution deviate from ideal behavior, the value of the activity coefficient decreases, and the concentrations of the ions do not approximate their activities. Under these conditions, the concentrations do not reflect the behavior of the dissolution equilibrium, and the equation cannot be used for precipitation or solubility calculations. More complex estimations of activity coefficients must be made and applied to the general equation (Birkett et al., 1988, pp. 2.6-1 to 2.6-24). Generally, radiochemical separations use an excess of a precipitating agent. The exact solution concentrations do not need to be known but they should be high to ensure compete reaction. Practical radiochemical separations performed based on solubility (either K_{sp} or coprecipitation phenomenon) are best described by M.L. Salutsky (1959, pp. 744-755).

Analysts often need to know if a precipitate will form when two solutions are mixed. For example:

> "If a chemist mixes 100 mL of 0.0050 M NaCl with 200 mL of 0.020 M $Pb(NO_3)_2$, will lead chloride precipitate? The *ion product,* Q, must be calculated and compared to K_{sp} for the process:

$$PbCl_2(s) \rightarrow Pb^{+2}(soln) + 2Cl^{-}(soln)$$

After the two solutions are mixed, $[Pb^{+2}] = 1.3 \times 10^{-2}$ M (0.2 L x 2.0×10^{-2} M/0.3 L), and $[Cl^-] = 1.7 \times 10^{-3}$ M (0.1 L x 5.0×10^{-3} M/0.3 L). The value for the ion product is calculated from the expression

$$Q = [Pb^{+2}][Cl^-]^2 \text{ or } [1.3 \times 10^{-2}][1.7 \times 10^{-3}]^2$$

$$Q = 3.8 \times 10^{-8}$$

The numerical value for K_{sp} is 1.6×10^{-5}. Because the ion product Q is less than K_{sp}, no precipitate will form. Only when the ion product is greater than K_{sp} will a precipitate form."

Conditions in the solution phase can affect solubility. For example, the solubility of an ion is lower in an aqueous solution containing a common ion, one of the ions comprising the compound, than in pure water because a precipitate will form if the K_{sp} is exceeded. This phenomenon is known as the *common ion effect* and is consistent with LeChatelier's Principle. For example, the presence of soluble sodium carbonate (Na_2CO_3) in solution with strontium ions can cause the precipitation of strontium carbonate, because carbonate ions from the sodium salt contribute to their overall concentration in solution and tend to reverse the solubility equilibrium of the "insoluble" strontium carbonate:

$$Na_2CO_3(s) \rightarrow 2\ Na^{+1}(soln) + CO_3^{-2}(soln)$$

$$SrCO_3(s) \rightarrow Sr^{+2}(soln) + CO_3^{-2}(soln)$$

Alternatively, if a complexing agent or ligand is available that can react with the cation of a precipitate, the solubility of the compound can be markedly enhanced. An example from Section 14.3.4.3, "Formation and Dissolution of Precipitates," provides an illustration of this phenomenon. In the determination of ^{90}Sr, Sr^{+2} is separated from the bulk of the solution by direct precipitation of the sulfate ($SrSO_4$). The precipitate is redissolved by forming a complex ion with EDTA, $Sr(EDTA)^{-2}$, to separate it from lanthanides and actinides (DOE, 1994, Method RP520):

$$SrSO_4(s) \rightarrow Sr^{+2}(soln) + SO_4^{-2}(soln)$$

$$Sr^{+2}(soln) + EDTA^{-4} \rightarrow Sr(EDTA)^{-2}(soln)$$

Additionally, many metal ions are weakly acidic and hydrolyze in solution. Hydrolysis of the ferric ion (Fe^{+3}) a classical example of this phenomenon:

$$Fe^{+3} + H_2O \rightarrow Fe(OH)^{+2} + H^{+1}$$

When these metal ions hydrolyze, producing a less soluble complex, the solubility of the salt is a function of the pH of the solution, increasing as the pH decreases. The minimum solubility is found under acidic conditions when the concentrations of the hydrolyzed species become negligible. As demonstrated by Leussing, the solubility of a salt also depends upon the activity of the solid phase. There are a number of factors that affect the activity of the solid phase (Leussing, 1959, pp. 690-692):

- *Polymorphism* is the existence of a chemical substance in two or more crystalline forms. For example, calcium carbonate can have several different forms; only one form of a crystal is stable at a given temperature. At ordinary pressures and temperatures, calcite with a solubility of 0.028 g/L, is the stable form. Aragonite, another common form of calcium carbonate ($CaCO_3$), has a solubility of 0.041g/L at these conditions. It is not necessarily calcite that precipitates when solutions of sodium carbonate and calcium nitrate are mixed. Extremely low concentrations of large cations, such as strontium, barium, or lead, promote the precipitation of aragonite over calcite (Wray and Daniels, 1957). On aging, the more soluble aragonite converts to calcite.

- Various possible hydrates of a solid have different solubilities. For instance, at 25 °C, the molar solubility of gypsum ($CaSO_4 \cdot 2H_2O$) is 0.206 and that of anhydrite ($CaSO_4$) is 0.271.

- The solid phase can undergo a reaction with a salt in solution.

- Particle size of a solid can affect its solubility, because it has been demonstrated that the solubility of smaller particles is greater than that of larger particles.

- Age of a precipitate can affect solubility. For example, Biederman and Schindler (1957) have demonstrated that the solubility of precipitated ferric hydroxide [$Fe(OH)_3$] undergoes a four-fold decrease to a steady state after 200 hours.

- Exchange of ions at the surface of the crystal with ions in the solution can affect the solubility of a solid. This effect is a function of the amount of surface available for exchange and is, therefore, greater for a finely divided solid. For example, Kolthoff and Sandell (1933) observed that calcium oxalate (CaC_2O_4) can exchange with either sulfate or barium ions:

$$CaC_2O_4(s) + SO_4^{-2}(soln) \rightarrow CaSO_4(s) + C_2O_4^{-2}(soln)$$

$$CaC_2O_4(s) + Ba^{+2}(soln) \rightarrow BaC_2O_4(s) + Ca^{+2}(soln)$$

The excess of common ions that appears on the right-hand side of the equations represses the solubility of calcium oxalate according to the laws of mass action.

Ideally, separation of common ions from foreign ions in solution by precipitation will result in a pure solid that is easy to filter. This method should ensure the production of a precipitate to meet these criteria as closely as possible. The physical process of the formation of a precipitate is quite complex, and involves both nucleation and crystal growth. *Nucleation* is the formation within a supersaturated solution of the smallest particles of a precipitate (nuclei) capable of spontaneous growth. The importance of nucleation is summarized by Salutsky (1959, p. 734):

> "The nucleation processes govern the nature and purity of the resulting precipitates. If the precipitation is carried out in such a manner as to produce numerous nuclei, precipitation will be rapid, individual crystals will be small, filtration and washing difficult, and purity low. On the other hand, if precipitation is carried out so that only a few nuclei are formed, precipitation will be slower, crystals larger, filtration easier, and purity higher. Hence, control of nucleation processes is of considerable significance in analytical chemistry."

Once the crystal nuclei are formed, crystal growth proceeds through diffusion of the ions to the surface of the growing crystal and deposition of those ions on the surface. This crystal growth continues until supersaturation of the precipitating material is eliminated and equilibrium solubility is attained.

Thus, the goal is to produce fewer nuclei during precipitation so that the process will occur slowly, within reasonable limits, and larger crystals will be formed. Impurities result from three mechanisms: (1) inclusion, either by isomorphous replacement (isomorphic inclusion), replacement of a common ion in the crystal structure by foreign ions of similar size and charge to form a mixed crystal, or by solid solution formation (nonisomorphic inclusion), simultaneous crystallization of two or more solids mixed together; (2) surface absorption of foreign ions; and (3) occlusion, the subsequent entrapment of adsorbed ions as the crystal grows. Slow growth gives the isomorphous ion time to be replaced by a common ion that fits the crystal structure perfectly, producing a more stable crystal. It also promotes establishment of equilibrium conditions for the formation of the crystal structure so that adsorbed impurities are more likely to desorb and be replaced by a common ion rather than becoming entrapped. In addition, for a given weight of the solid that is forming, a small number of large crystals present an overall smaller surface area than a large number of small crystals. The large crystals provide less surface area for impurities to adsorb.

14.8.3.2 Factors Affecting Precipitation

Several factors affect the nature and purity of the crystals formed during precipitation. A knowledge of these factors permits the selection and application of laboratory procedures that increase the effectiveness of precipitation as a technique for the separation and purification of ions, and for the formation of precipitates that are easily isolated. These factors, summarized from Berg (1963, pp. 251-284) and Salutsky (1959, pp. 736-742), include the following:

- *Rate of precipitation.* Formation of large, well-shaped crystals is encouraged through slow precipitation because fewer nuclei form and they have time to grow into larger crystals to the detriment of smaller crystals present. Solubility of the larger crystals is less than that of smaller crystals because smaller crystals expose more surface area to the solution. Larger crystals also provide less surface area for the absorption of foreign ions. Slow precipitation can be accomplished by adding a very dilute solution of the precipitant gradually, with stirring, to a medium in which the resulting precipitate initially has a moderate solubility.

- *Concentration of Ions and Solubility of Solids.* The rate of precipitation depends on the concentration of ions in solution and the solubility of the solids formed during the equilibrium process. A solution containing a low concentration of ions, but sufficient concentration to form a precipitate, will slow the process, resulting in larger crystal formation. At the same time, increasing the solubility of the solid, either by selecting the counter-ion for precipitation or by altering the precipitating conditions, will also slow precipitation. Many radionuclides form insoluble solids with a variety of ions, and the choice of precipitating agent will affect the solubility of the precipitate. For example, radium sulfate ($RaSO_4$) is the most insoluble radium compound known. Radium carbonate ($RaCO_3$) is also insoluble, but its K_{sp} is greater than that of radium sulfate (Kirby and Salutsky, 1964, p. 9).

- *Temperature.* Precipitation at higher temperature slows nucleation and crystal growth because of the increased thermal motion of the particles in solution. Therefore, larger crystals form, reducing the amount of adsorption and occlusion. However, most solids are more soluble at elevated temperatures, effectively reducing precipitate yield; an optimum temperature balances these opposing factors.

- *Digestion.* Extremely small particles, with a radius on the order of one micron, are more soluble than larger particles because of their larger surface area compared to their volume (weight). Therefore, when a precipitate is heated over time (*digestion*) the small crystals dissolve and larger crystals grow (*Ostwald ripening*). Effectively, the small crystals are recrystallized, allowing the escape of impurities (occluded ions) and growth of larger crystals.

This process reduces the surface area for adsorption of foreign ions and, at the same time, replaces the impurities with common ions that properly "fit" the crystal lattice. Recrystallization perfects the crystal lattice, producing a purer precipitate (see *Reprecipitation* below). Digestion is used in an ^{131}I determination to increase the purity of the lead iodide (PbI_2) crystals (EPA, 1984, pp. I-01-1-9).

- *Degree of Supersaturation.* A relatively high degree of supersaturation is required for spontaneous nucleation, and degree of supersaturation is the main factor in determining the physical character of a precipitate. Generally, the higher the supersaturation required, the more likely a curdy, flocculated colloid will precipitate because more nuclei form under conditions of higher supersaturation and crystal growth is faster. In contrast, the lower the supersaturation required, the more likely a crystalline precipitate will form because fewer nuclei form under these conditions and crystal growth is slower. Most perfect crystals are formed, therefore, from supersaturated solutions that require lower ion concentrations to reach the necessary degree of supersaturation and, as a result, inhibit the rate of nucleation and crystal growth. Degree of supersaturation ultimately depends on physical properties of the solid that affect its formation. Choice of counter-ion will determine the type of solid formed from a radionuclide, which, in turn, determines the degree of saturation required for precipitation. Many radionuclides form insoluble solids with a variety of ions, and the choice of precipitating agent will affect the nature of the precipitate.

- *Solvent.* The nature of the solvent affects the solubility of an ionic solid (precipitate) in the solvent. The polarity of water can be reduced by the addition of other miscible solvents such as alcohols, thereby reducing the solubility of precipitates. Strontium chromate ($SrCrO_4$) is soluble in water, but it is insoluble in a methyl alcohol (CH_3OH)-water mixture and can be effectively precipitated from the solution (Berg, 1963, p. 364). In some procedures, precipitation is achieved by adding alcohol to an aqueous solution, but the dilution effect might reduce the yield because it lowers the concentration of ions in solution.

- *Ion Concentration.* The common-ion effect causes precipitation to occur when the concentration of ions exceeds the solubility-product constant. In some cases, however, excess presence of common ions increases the solubility of the precipitate by decreasing the activity of the ions in solution, as they become more concentrated in solution and deviate from ideal behavior. An increase in concentration of the ions is necessary to reach the activity of ions necessary for precipitate formation.

- *Stirring.* Stirring the solution during precipitation increases the motion of particles in solution and decreases the localized buildup of concentration of ions by keeping the solution

thoroughly mixed. Both of these properties slow nucleation and crystal growth, thus promoting larger and purer crystals. This approach also promotes recrystallization because the smaller crystals, with their net larger surface area, are more soluble under these conditions. Virtually all radiochemical laboratories employ stirring with a magnetic stirrer during precipitation reactions.

- *Complex-Ion Formation.* Formation of complex ions can be used to *hold back* impurities from precipitating by producing a more soluble form of a solid. The classical example of this phenomenon is the precipitation of lead (Pb^{+2}) in the presence of silver ions (Ag^{+1}). Chloride ion (Cl^{-1}) is the precipitating agent that produces insoluble lead chloride ($PbCl_2$). In an excess of the agent, silver chloride (AgCl) is not formed because a soluble salt containing the complex ion, $AgCl_2^{-1}$ is formed. Complex-ion formation is also used to form precipitates (see Section 14.3, "Complexation").

- *pH Effect.* Altering the pH of aqueous solutions will alter the concentration of ions in the precipitation equilibrium by the common-ion effect, if the hydrogen ion (H^{+1}) or hydroxide ion (OH^{-1}) is common to the equilibrium. For example, calcium oxalate (CaC_2O_4) can be precipitated or dissolved, depending on the pH of the solution, as follows:

$$Ca^{+2} + C_2O_4^{-2} \rightarrow CaC_2O_4$$

Because the oxalate concentration is affected by the hydrogen-ion concentration,

$$H^{+1} + C_2O_4^{-2} \rightarrow HC_2O_4^{-1},$$

increasing the hydrogen-ion concentration (lowering the pH) decreases the oxalate ion concentration by forming bioxalate, which makes the precipitate more soluble. Therefore, decreasing the hydrogen-ion concentration (raising the pH), therefore, aids precipitation. Similar effects are obtained with carbonate precipitates:

$$Sr^{+2} + CO_3^{-2} \rightarrow SrCO_3$$

$$H^{+1} + CO_3^{-2} \rightarrow HCO_3^{-1}$$

Many metal sulfides are formed in a solution of hydrogen sulfide by generating the sulfide ion (S^{-2}) at suitable pH:

$$H_2S \rightarrow H^{+1} + HS^{-1}$$

$$HS^{-1} \rightarrow H^{+1} + S^{-2}$$

$$Pb^{+2} + S^{-2} \rightarrow PbS$$

The pH can also influence selective formation of precipitates. Barium chromate will precipitate in the presence of strontium at pH 4 to 8, leaving strontium in solution. Sodium carbonate is added and strontium precipitates after ammonia (NH_3) is added to make the solution more alkaline. This procedure is the basis for the separation of radium from strontium in the radioanalysis of strontium in drinking water (EPA, 1980, p. 63).

- *Precipitation from Homogeneous Solution.* Addition of a precipitating agent to a solution of ions causes a localized excess of the reagent (higher concentrations) to form in the mixture. The excess reagent is conducive to rapid formation of a large number of small crystals, producing a precipitate of imperfect crystals that contains excessive impurities. The precipitate formed under these conditions is sometimes voluminous and difficult to filter. Localized excesses can also cause precipitation of more soluble solids than the expected precipitate.

These problems largely can be avoided if the solution is homogenous in all stages of precipitate formation, and if the concentration of precipitating agent is increased, as slowly as practical, to cause precipitation from the most dilute solution possible. This increase in concentration is accomplished, not by adding the precipitating agent directly to the solution, but rather by generating the agent throughout the solution, starting with a very small concentration and slowly increasing the concentration while stirring. The precipitating agent is generated indirectly as the result of a chemical change of a reagent that produces the precipitating agent internally and homogeneously throughout the solution. The degree of supersaturation is low because the concentration of precipitating agent in solution is always uniformly low enough for nucleation only. This method produces larger crystals with fewer impurities.

Table 14.11 (Salutsky, 1959, p. 741) summarizes methods used for precipitate formation from homogeneous solution. Descriptions of these methods can be found in Gordon et al. (1959).

Some agents are generated by decomposition of a compound in solution. Hydrogen sulfide, for example, is produced from thioacetamide:

$$CH_3CSNH_2 + 2\ H_2O \rightarrow CH_3COO^{-1} + H_2S + NH_4^{+1}$$

Copper sulfide (CuS) coprecipitates technetium from a homogeneous medium by the generation of hydrogen sulfide by this method (EPA, 1973, pp. 67-72). Other agents alter the pH of the solution (see "pH Effect" above). Hydrolysis of urea, for example, produces ammonia, which raises the pH of a solution:

$$H_2NCONH_2 + H_2O \rightarrow CO_2 + 2\ NH_3$$

TABLE 14.11 — Summary of methods for utilizing precipitation from homogeneous solution[1]

Precipitant	Reagent	Element Precipitated
Hydroxide	Urea	Al, Ga, Th, Fe(III), Sn, and Zr
	Acetamide	Ti
	Hexamethylenetetraamine	Th
	Metal Chelate and H_2O_2	Fe(III)
Phosphate	Triethyl Phosphate	Zr and Hf
	Trimethyl Phosphate	Zr
	Metaphosphoric Acid	Zr
	Urea	Mg
Oxalate	Dimethyl Oxalate	Th, Ca, Am, Ac, and Rare Earths
	Diethyl Oxalate	Mg, Zn, and Ca
	Urea and an Oxalate	Ca
Sulfate	Dimethyl Sulfate	Ba, Ca, Sr, and Pb
	Sulfamic Acid	Ba, Pb, and Ra
	Potassium Methyl Sulfate	Ba, Pb, and Ra
	Ammonium Persulfate	Ba
	Metal Chelate and Persulfate	Ba
Sulfide	Thiocetamide	Pb, Sb, Bi, Mo, Cu, and As, Cd, Sn, Hg, and Mn
Iodate	Iodine and Chlorate	Th and Zr
	Periodate and Ethylene Diacetate (or ß-Hydroxy Acetate)	Th and Fe(III)
	Ce(III) and Bromate	Ce(IV)
Carbonate	Trichloroacetate	Rare Earths, Ba, and Ra
Chromate	Urea and Dichromate	Ba and Ra
	Potassium Cyanate and Dichromate	Ba, Ra
	Cr(III) and Bromate	Pb
Periodate	Acetamide	Pb
Chloride	Silver Ammonia Complex and ß-Hydroxyethyl Acetate	Ag
Arsenate	Arsenite and Nitrite	Zr

Precipitant	Reagent	Element Precipitated
Tetrachlorophthalate	Tetrachlorophthalic Acid	Th
Dimethylgloxime	Urea and Metal Chelate	Ni
8-Hydroxyquinoline	Urea and Metal Chelate	Al
Fluoride	Fluoroboric Acid	La

(1) Salutsky, 1959, p. 741

- *Reprecipitation.* This approach increases the purity of precipitates. During the initial precipitation, crystals collected contain only a small amount of foreign ions relative to the common ions of the crystal. When the precipitate is redissolved in pure solvent, the foreign ions are released into solution, producing a concentration of impurities much lower than that in the original precipitating solution. On reprecipitation, a small fraction of impurities is carried down with the precipitate, but the relative amount is much less than the original because their concentration in solution is less. Nevertheless, foreign ions are not eliminated because absorption is greater at lower, rather than at higher, concentrations. On balance, reprecipitation increases the purity of the crystals. Reprecipitation is used in the procedure to determine americium (Am) in soil (DOE, 1990 and 1997, Method Am-01). After americium is coprecipitated with calcium oxalate (CaC_2O_4), the precipitate is reprecipitated to purify the solid.

14.8.3.3 Optimum Precipitation Conditions

There is no single, fixed rule to eliminate all impurities during precipitation (as discussed in the section above), but over the years, a number of conditions have been identified from practical experience and theoretical considerations that limit these impurities (Table 14.12). Precipitations are generally carried out from dilute solutions adding the precipitant slowly with some form of agitation to a hot solution. Normally, the precipitant is then allowed to age before it is removed by filtration and washed. Reprecipitation is then commonly performed. Reprecipitation is one of the most powerful techniques available to the analyst because it increases purity, regardless of the form of the impurity.

Table 14.12 highlights the optimum precipitation conditions to eliminate impurities.

TABLE 14.12 — Influence of precipitation conditions on the purity of precipitates [1, 2]

Condition	Form of Impurity			
	Mixed Crystals	Surface Adsorption	Occlusion and Inclusion	Post-precipitation
Dilute solutions	o	+	+	o
Slow precipitation	+	+	+	-
Prolonged digestion	-	+	+	-
High temperature	-	+	+	-
Agitation	+	+	+	o
Washing the precipitate	o	+	o	o
Reprecipitation	+	+	+	o

(1) +, increased purity; -, decreased purity; o, little or no change in purity
(2) Salutsky, 1959, p. 764

14.8.4 Coprecipitation

In many solutions, especially those of environmental samples, the concentration of the radionuclide of interest is too low to cause precipitation, even in the presence of high concentrations of its counter-ion, because the product of the concentrations does not exceed the solubility product. Radium in most environmental samples, for example, is not present in sufficient concentration to cause its very insoluble sulfate ($RaSO_4$) to precipitate. The radionuclide can often be brought down selectively and quantitatively from solution during precipitation of an alternate insoluble compound by a process called *coprecipitation.* The insoluble compound commonly used to coprecipitate radium isotopes in many radioanalytical procedures is another insoluble sulfate, barium sulfate ($BaSO_4$) (EPA, 1984, Method Ra-01; EPA, 1980, Method 900.1). The salt is formed with barium, also a member of the alkaline earth family of elements with chemical properties very similar to those of radium. Alternatively, a different salt that is soluble for the radionuclide can be used to cause coprecipitation. Radium can be coprecipitated with lanthanum fluoride, even though radium fluoride is soluble itself. For trace amounts of some radionuclides, other isotopic forms of the element are available that can be added to the solution to bring the total concentration of all forms of the element to the level that will result in precipitation. For trace quantities of ^{90}Sr, inactive strontium (^{85}Sr), which will not interfere with the radioanalysis of ^{90}Sr, is added to permit the precipitation of strontium carbonate in the presence of carbonate ions. The added ion that is present in sufficient concentration to cause a precipitate to form is called a carrier (Section 14.9, "Carriers and Tracers"). Barium, lanthanum, and stable strontium, respectively, are carriers in these examples (DOE, 1995, Method RP5001; DOE, 1990 and 1997, Method Sr-02; EPA, 1984, Sr-04). The

term carrier is also used to designate the insoluble compound that causes coprecipitation. Barium sulfate, lanthanum fluoride (LaF_3), and strontium carbonate are sometimes referred to as the carrier in these coprecipitation procedures. See Wahl and Bonner (1951, p. 403) for additional examples of tracers and their carriers used for coprecipitation.

The common definition of coprecipitation is, "the contamination of a precipitate by substances that are normally soluble under the conditions of precipitation" (Salutsky, 1959, p. 748). In a very broad sense, coprecipitation is alternately defined as the precipitation of one compound simultaneously with one or more other compounds to form mixed crystals (Berg, 1963, p. 296). Each is present in macro concentrations (i.e., sufficient concentrations to exceed the solubility product of each). As the term is used in radiochemistry, coprecipitation is the simultaneous precipitation of one compound that is normally soluble under the conditions of precipitation with one or more other compounds that form a precipitate under the same conditions. Coprecipitation of two or more rare earths as oxalates, barium and radium as sulfates, or zirconium (Zr) and hafnium (Hf) as phosphates are examples of this broader definition (Salutsky, 1959, p. 748). By either definition, coprecipitation introduces foreign ions into a precipitate as impurities that would normally be expected to remain in solution; and precipitation techniques, described in the previous section, are normally used to maximize this effect while minimizing the introduction of true impurities. As a method to separate and collect radionuclides present in solution at very low concentration, coprecipitation is performed in a controlled process to associate the ion of choice selectively with a precipitate, while excluding other foreign ions that would interfere with the analytical procedure.

14.8.4.1 Coprecipitation Processes

In order to choose the best conditions to coprecipitate an ion selectively, two processes should be considered. First is precipitation itself and the appropriate techniques employed to minimize association of impurities (see Section 14.8.3). Second is coprecipitation mechanisms and the controlling factors associated with each. Three processes (described above in Section 14.8.3.1, "Solubility and the Solubility Product Constant") are responsible for coprecipitation, although the distinction between these processes is not always clear (Hermann and Suttle, 1961, p. 1369). They consist of: (1) inclusion, i.e., uptake from solution of an ion similar in size and charge to the solid forming the precipitate in order to form a mixed crystal or solid solution; (2) surface adsorption; and (3) occlusion (mechanical entrapment).

Inclusion. If coprecipitation is accomplished from a homogeneous solution allowing the crystals to form slowly in an orderly manner, then inclusion contributes to the coprecipitation process.

Under these conditions, the *logarithmic distribution law* applies, which represents the most efficient coprecipitation method that involves mixed crystals (Salutsky, 1959, p. 750):

$$\log(I_i/I_f) = \lambda \log(P_i/P_f)$$

In the equation, I_i is the concentration of impurity in solution at the start of crystallization and I_f is the concentration at the end. P represents the corresponding concentration of the primary ion in solution. Lambda, λ, is the *logarithmic distribution coefficient* and is a constant. Values of λ for some tracers distributed in solid carriers can be found in Wahl and Bonner (1951, p. 393). Lambda values greater than one represent removal of a foreign ion by inclusion during coprecipitation. The larger the value of lambda, the more effective and selective for a specific ion the process is. Lambda is also inversely proportional to the rate of precipitation. Slow precipitation, as accomplished by homogeneous precipitation, results in larger values and more efficient coprecipitation. For example, "Actinium [Ac] has been selectively removed from solutions containing iron and aluminum [Al] through slow oxalate precipitation by the controlled hydrolysis of dimethyl oxalate" (Hermann and Suttle, 1961, p. 1376). Also, as described in Section 14.8.3.2, "Factors Affecting Precipitation," technetium is coprecipitated with copper sulfide (CuS) carrier produced by the slow generation of hydrogen sulfide (H_2S) as thioacetamide is hydrolyzed in water (EPA, 1973, pp. 67-72).

Generally, λ decreases as the temperature increases; thus, coprecipitation by inclusion is favored by lower temperature.

Digestion of the precipitate at elevated temperature over lengthy time periods—a process that promotes recrystallization and purer crystals—will often cause mixed crystals to form by an alternate mechanism (i.e., *homogeneous distribution*) that is not as efficient, but which is often as successful as logarithmic distribution. The *equilibrium distribution law* is represented by (Salutsky, 1959, p. 749):

$$(I/P)_{ppt.} = D\,(I/P)_{soln.}$$

where I represents the amount of impurity and P the amount of primary substance forming the precipitate. The symbol *D* is the *homogeneous distribution coefficient*. Values of D greater than one represent removal of a foreign ion by inclusion during coprecipitation. Some values of D can be found in Wahl and Bonner (1951, p. 393). According to Hermann and Suttle:

> "Homogeneous distribution is conveniently obtained at ordinary temperatures by rapid crystallization from supersaturated solutions with vigorous stirring. Under such conditions

> the precipitate first formed is very finely divided, the recrystallization of the minute crystals is rapid, and each molecule (sic) passes many times between solution and precipitate. If this process is repeated often enough, an equilibrium between solid and solution is obtained, and all the resulting crystals grow from a solution of constant composition" (Hermann and Suttle, 1961, pp. 1473-1474).

In either case, optimal results are obtained through inclusion when the precipitate contains an ion with chemical properties similar to those of the foreign ion, although it is not necessary for the similarity to exist in every successful coprecipitation. Barium sulfate is very successful in coprecipitating Ra^{+2}, primarily because radium is in the same chemical family as barium, and has the same charge and a similar ionic radius. For best results, the radius of the foreign ion should be within approximately 15 percent of that of one of the common ions in the precipitate (Hermann and Suttle, 1961, p. 1479).

Surface Adsorption. During surface adsorption, ions are adsorbed from solution onto the surfaces of precipitated particles. The conditions leading to surface adsorption are described by Salutsky:

> "The surface of a precipitate is particularly active. Ions at the surface of a crystal (unlike those within the crystal) are incompletely coordinated and, hence are free to attract other ions of opposite charge from solution" (Salutsky, 1959, p. 754).

Adsorption involves a primary adsorption layer that is held very tightly, and a counter-ion layer held more loosely. Ions common to the precipitate are adsorbed most strongly at the surface to continue growth of the crystal. During precipitation of $BaSO_4$, barium ions (Ba^{+2}) and sulfate ions (SO_4^{-2}) are the primary ions adsorbed. If only one of the common ions remains in solution, then foreign ions of the opposite charge are adsorbed to maintain electrical neutrality. When barium sulfate is precipitated from a solution containing excess barium ions, for example, foreign ions such as Cl^{-1}, if present, are adsorbed after sulfate ions are depleted in the precipitation process. Foreign ions of the same charge, such as Na^{+1}, are repelled from the surface. Surface adsorption can be controlled, therefore, by controlling the concentration of ions during precipitation or by the addition of ions to alter the concentration. A precipitate of silver chloride (AgCl) in excess Ag^{+1} repels $^{212}Pb^{+2}$, but in a solution containing an equal quantity of the common silver and chloride ions, approximately 2 percent of ^{212}Pb is adsorbed (Salutsky, 1959, pp. 754-755). In contrast, almost 86 percent of ^{212}Pb is adsorbed if an iodide solution is added to precipitate the silver ions as silver iodide (AgI), thereby reducing the concentration of silver ions and making the chloride ion in excess in the solution. According to the *Paneth-Fajans-Hahn adsorption rule*, the ion most adsorbed will be the one that forms the least soluble compound with an ion of the precipitate. For example, barium sulfate in contact with a solution containing excess sulfate ions

will adsorb ions of Pb > Ca > K > Na, which reflects the order of solubility of the respective sulfates: thus, $PbSO_4 < CaSO_4 < K_2SO_4 < Na_2SO_4$ (Salutsky, 1959, p. 755).

"Because adsorption is a surface phenomenon, the larger the surface area of a precipitate, the greater the adsorption of impurities" (Salutsky, 1959, p. 755). For that reason, colloidal crystals exhibit a high degree of nonspecific adsorption. When a colloid is flocculated by the addition of an electrolyte, the electrolyte can be adsorbed as an impurity. This interference largely can be eliminated by aging the precipitate, thereby growing larger crystals and reducing the surface area. Additionally, nonvolatile impurities can be replaced on the particle by washing the colloidal precipitate with a dilute acid or ammonium salt solution. Well-formed large crystals exhibit much less adsorption, and adsorption is not a significant factor in coprecipitation with these solids. The tendency for a particular ion to be adsorbed depends on, among other factors, charge and ionic size (Berg, 1963, p. 299). Large ions with a high charge exhibit high adsorption characteristics: a high ionic charge increases the electrostatic attraction to the charged surface, and an ion with a large radius is less hydrated by the solution and not as attracted to the solution phase.

"The amount of adsorption is also affected by prolonged standing of the precipitate in contact with the solution. The fraction adsorbed is higher for some tracer ions, while the fraction is lower for others. Recrystallization occurring during standing decreases the surface area so that the fraction of tracer carried will decrease unless the tracer is trapped in the growing crystals ... in which case the fraction carried may increase." (Wahl, 1951, p. 117).

Adsorption also depends on the concentration of an ion in solution (Berg, 1963, p. 299). A high concentration of impurity increases the probability of solute interaction at the solid surface and favors adsorption. Salutsky comments on the percent adsorption:

> "Generally, the percent adsorption is much greater at low concentrations than at high concentrations. At very high concentrations of impurity, adsorption reaches a maximum value, i.e., the adsorption is saturated" (Salutsky, 1959, pp. 755-756).

Occlusion. Occlusion of an impurity within a precipitate results when the impurity is trapped mechanically by subsequent crystal layers. For that reason, occluded impurities cannot be physically removed by washing. Occlusion is more prevalent with colloidal precipitates than with large crystals because of the greater surface area of colloidal solids. Freshly prepared hydroxides and sulfides commonly contain occluded impurities, but most of them are released upon aging of the precipitate.

Mechanical entrapment occurs particularly when the precipitating agent is added directly to a solution. Because of the localized high concentrations of precipitant, impurities are precipitated that become occluded by the subsequent precipitation of the primary substance. The speed of the precipitation process also affects the extent of occlusion. Occlusion can be reduced, therefore, by homogeneous precipitation. Coprecipitation of strontium by barium sulfate, for example, is accomplished by the homogeneous generation of sulfate by the hydrolysis of dimethylsulfate, $(CH_3)_2SO_4$ (Hermann and Suttle, 1961, p. 1480). Digestion also eliminates occluded particles as the solid is recrystallized. Considerable occlusion occurs during nucleation, and, therefore, reducing the precipitation rate by lowering the temperature and reducing the number of nuclei formed reduces the initial coprecipitation by occlusion.

This type of coprecipitation is not limited to solid impurities. Sometimes the solvent and other impurities dissolved in the solvent become trapped between layers of crystals. This *liquid occlusion* is common in numbers of minerals such as quartz and gypsum.

14.8.4.2 Water as an Impurity

In addition to other impurities, all precipitates formed from aqueous solutions contain water (Salutsky, 1959, pp. 761-763). This water might be *essential water*, present as an essential part of the chemical composition (e.g., $MgNH_4PO_4 \cdot 6H_2O$, $Na_2CO_3 \cdot H_2O$), or it might be *nonessential water*. Nonessential water can be present in the precipitate as hygroscopic water, surface water, or included water. *Hygroscopic water* refers to the water that a solid adsorbs from the surrounding atmosphere. Many colloidal precipitates are highly hygroscopic because of their large surface areas. Moreover, water can be adsorbed to the surface of the precipitate or included within the crystal matrix, as described previously.

14.8.4.3 Postprecipitation

Postprecipitation results when a solution contains two ions, one that is rapidly precipitated and another that is slowly precipitated by the precipitating agent (Kolthoff et al., 1969, p. 245). The first precipitate is usually contaminated by the second one. For example, calcium oxalate is a moderately insoluble compound that can be precipitated quantitatively with time. Because the precipitation tends to be slow, the precipitate is allowed to remain in contact with the solution for some time before filtering. Magnesium oxalate is too soluble to precipitate on its own under normal conditions. As long as the solution contains a predominance of calcium ions, very little magnesium precipitates. However, as the precipitation of calcium approaches quantitative levels, the competition of calcium and magnesium ions for adsorption at the surface becomes more intense. As time progresses, the magnesium oxalate adsorbed on the surface acts as seed to

induce the post-precipitation of a second solid phase of magnesium oxalate (MgC_2O_4). Once precipitated, the magnesium oxalate is only slightly soluble and does not redissolve.

14.8.4.4 Coprecipitation Methods

Selective coprecipitation of a radionuclide with an insoluble compound is primarily accomplished by the judicious selection of the compound that forms the precipitate and the concentration of solutions used in the precipitate's formation. Using good precipitation technique minimizes the coprecipitation of impurities. The compound, then, should maximize coprecipitation of the select radionuclide while providing a well-formed solid that attracts a minimum of other foreign ions as impurities. In general, conditions that favor precipitation of a substance in macroamounts also favor the coprecipitation of the same material from tracer concentrations (i.e., too low for precipitate formation) with a foreign substance (Friedlander et al., 1981, p. 294). Wahl and Bonner provide a useful summary for coprecipitation of a tracer by a carrier:

> "In general a tracer is efficiently carried by an ionic precipitate if: (1) the tracer ion is isomorphously incorporated into the precipitate, or (2) the tracer ion forms a slightly soluble or slightly dissociated compound with the oppositely charged lattice ion and if the precipitate has a large surface with charge opposite to that of the tracer ion (i.e., presence of excess of the oppositely charged lattice ion)" (Wahl and Bonner, 1951, p. 105).

Considering the principles of precipitation and coprecipitation, radium is coprecipitated quantitatively with barium sulfate using excess sulfate in solution because: (1) radium forms the least soluble sulfate of the other elements in the alkaline earth family (Paneth-Fajans-Hahn adsorption rule); (2) the radium ion carries the same charge as the barium ion and is very similar in size (inclusion); and 3) an excess of sulfate preferentially creates a common-ion layer on the crystalline solid of sulfate ions that attracts barium ions and similar ions such as radium (absorption). For example, in a procedure to determine ^{226}Ra in water samples, radium is coprecipitated as barium sulfate using 0.36 moles of sulfate with 0.0043 moles of barium, a large excess of sulfate (EPA, 1984, Method Ra-03).

The isolation of microquantities of tracers often occurs in two steps: first the tracer is separated by coprecipitation with a carrier, and then it is separated from the carrier (Hermann and Suttle, 1961, p. 1486). Use of carriers that can be easily separated from the tracer is helpful, therefore, coprecipitation by inclusion is not generally used. Coprecipitation by surface adsorption on unspecific carriers is the most common method employed. Manganese dioxide MnO_2, sulfides (MnS), and hydroxides [$Mn(OH)_2$] are important nonspecific carries because of their high surface

areas. Ferric hydroxide [$Fe(OH)_3$] is very useful for adsorbing cations, because it forms a very finely divided precipitate with a negative charge in excess hydroxide ion. Ferric hydroxide is used, for example, to collect plutonium in solution after it has been isolated from tissue (DOE, 1990 and 1997, Method Pu-04). Tracers can be separated by dissolving the solid in acid and extracting the iron in ether.

> "The amount of ion adsorbed depends on its ability to compete with other ions in solution. Ions capable of displacing the ions of the radioelements are referred to as holdback carriers (see Section 14.9.2.4, *Holdback Carriers*). Highly charged ions, chemical homologs, and ions isotopic with the radioelement are among the most efficient displacers. Thus, the addition of a little inactive strontium makes it possible to precipitate radiochemically pure radiobarium as the nitrate or chloride in the presence of radiostrontium" (Hermann and Suttle, 1961, p. 1487)

Tables 14.13 and 14.14 provide more details about common coprecipitating agents for radionuclides.

TABLE 14.13 — Common coprecipitating agents for radionuclides[1]

Radionuclide	Oxidation State	Coprecipitate	Carrier[2]	Notes
Am	13	hydroxide	Am^{+3}, Fe^{+3}	
		iodate	Ce^{+4}, Th^{+4}, Zr^{+4}	
		fluoride, oxalate, phosphate, hydroxide	La^{+3}, Ce^{+3}, Nd^{+3}, Bi^{+3}	
		oxalate	Ca^{+2}	
		acetate	Am^{+4}	
		fluoride, sulfate	La^{+3}	
		acetate	UO_2^{+2}	
Cs	+1	phosphomolybdate, chloroplatinate, bismuthnitrate, silicomolybdate	Cs^{+1}	
Co	+2	hydroxide	Co^{+2}	
		potassiumcobaltnitrate	Co^{+2}	
		1-nitroso-2-napthol	Co^{+2}	
		sulfide	Co^{+2}	
Fe	+3	hydroxide	Fe^{+3}	
		ammoniumpyrouranate	Fe^{+3}	
I	-1	iodide	Pb^{+2}, Ag^{+1}, Pd^{+2}	
Ni	+2	dimethylgloxime hydroxide	Ni^{+2}	
Nb	+5	hydroxide, phosphate	Nb^{+5}	

Radionuclide	Oxidation State	Coprecipitate	Carrier[2]	Notes
Po	+4	tellurium	Te	tellurate reduced with $SnCl_2$
		tellurate	Pb^{+2}	
		selenium	Se or Se^{-2}	
		dioxide	Mn^{+4}	
		hydroxide	Fe^{+3}, Al^{+3}, La^{+3}	
		sulfide	Cu^{+2}, Bi^{+2}, Pb^{+2}	
Pu	+3	fluoride	La^{+3}, Nd^{+3}, Ce^{+3}, Ca^{+2}	
	+4	sulfate	$La^{+3}(K^{+1})$	
	+6	fluoride	La^{+3}, Nd^{+3}, Ce^{+3}	
		oxalate, iodate	Th^{+4}	
		phosphate	Zr^{+2}, Bi^{+3}	
		sodium uranylacetate	UO_2^{+2}	
Ra	+2	hydroxide	Fe^{+3}	
		sulfate, chromate, chloride, bromide	Ba^{+2}	
		oxalate, phosphate	Th^{+4}, Ca^{+2}, Ba^{+2}	
		fluoride	La^{+3}	
Sr	+2	carbonate	Sr^{+2}, Ba^{+2}, Ca^{+2}	
		nitrate	Sr^{+2}, Ba^{+2}	
		chromate	Ba^{+2}	alkaline pH
		sulfate	Sr^{+2}, Ca^{+2}, Pb^{+2}	
		phosphate	Sr^{+2}	
		hydroxide	Fe^{+3}	
Tc	+4	hydroxide	Tc^{+4}, Fe^{+3}, Mn^{+2}	
	+7	chlorate, iodate, perruthenate, tetrafluoroborate	$(Phenyl)_4As^{+1}$	
		sulfide	Tc^{+7}, Re^{+7}, Cu^{+2}, Cd^{+2}	
Th	+4	hydroxide	Th^{+4}, La^{+3}, Fe^{+3}, Zr^{+3}, Ac^{+3}, Zn^{+2}	
		fluoride	Th^{+4}, La^{+3}, Nd^{+3}, Ce^{+3}	
		iodate	Th^{+4}, Zr^{+3}	
		phosphate, peroxide	Th^{+4}, Bi^{+3}	
		sulfate	Ba^{+2}	
		oxalate	Ca^{+2}	
U	+4	cupferron, pyrophosphate, phosphate, iodate, sulfate, oxalate	U^{+4}	
		fluoride	La^{+3}, Nd^{+3}	
	+5	phosphate	Zr^{+3}	
		sulfate	Ca^{+2}	
	+6	cupferron	U^{+6}	neutral solution
		pyrouranate	U^{+6}	from aqueous NH_3, many ions stay in solution as NH_3 complex

Radionuclide	Oxidation State	Coprecipitate	Carrier[2]	Notes
		phosphate	U^{+6}, Al^{+3}	
		peroxide	U^{+6}	Th^{+4}, Zr^{+3} also coprecipitate
		hydroxide	Fe^{+3}	without carbonate
		fluoride	Th^{+4}	
Zr^{+4}				

(1) Compiled from: Anders, 1960; Booman and Rein, 1962; Cobble, 1964; EPA, 1973; 1980; 1984; DOE, 1990, 1995, 1997; Finston and Kinsley, 1961, Grimaldi, 1961; Grindler, 1962; Hyde, 1960; Kallmann, 1961; Kallmann, 1964; Kirby and Salutsky, 1964; Metz and Waterbury, 1962; Sedlet, 1964; Sundermann and Townley, 1960; and Turekian and Bolter, 1966.

(2) If the radionuclide itself is listed, alternate isotopic forms are sometimes used as carriers to form the precipitate.

TABLE 14.14 — Coprecipitation behavior of plutonium and neptunium

Carrier Compound	Pu(III)	Pu(IV)	Pu(VI)	Np(IV)	Np(V)	Np(VI)
Hydroxides	C	C	C	C	C	C
Calcium fluoride	C	C		C		
Lanthanum fluoride	C	C	NC	C	C	NC
Barium sulfate	C	C	NC	C	NC	NC
Phosphates:						
Calcium phosphate	C	C		C		
Bismuth phosphate	C	C		C	NC	NC
Zirconium phosphate	NC	C	NC	C	NC	NC
Thorium pyrophosphate	NC	C	NC			
Thorium hypophosphate		C	NC			
U(IV) hypophosphate		C	NC			
Oxalates:						
Lanthanum oxalate	C	C	NC	NC		
Bismuth oxalate	C	C	NC			
Thorium oxalate	C	C	NC	C		
U(IV) oxalate	C	C	NC			
Iodates:						
Zirconium iodate		C	NC	C		
Ceric iodate		C	NC	C		
Thorium iodate		C	NC	C		NC
Sodium uranyl acetate	NC	NC	C	NC	Poor	C
Zirconium phenylarsenate	NC	C	NC	C	Poor	NC
Thorium peroxide		C		C		
Bismuth arsenate		C	NC	C		

"C" indicates nearly quantitative coprecipitation under proper conditions; "NC" indicates that coprecipitation can be made less than 1-2 percent under proper conditions. [Data compiled from Seaborg and Katz, Korkisch (1969), and the NAS-NS 3050, 3058 and 3060 monographs.]

14.8.5 Colloidal Precipitates

Many precipitates exhibit colloidal properties, especially when freshly formed (Salutsky, 1959, p. 744). The term "colloid state" refers to the dispersion of one phase that has colloidal dimensions (less than one micrometer, but greater than one nanometer) within a second phase. A *colloidal solution* is a colloid in which the second phase is a liquid (also known as a *sol*). However, in radiochemistry, a colloid refers to the dispersion of solid particles in the solution phase. The mixture is not a true solution: particles of the dispersed phase are larger than typical ions and molecules, and can often be viewed by a light microscope. Colloidal precipitates are usually avoided in analytical procedures because they are difficult to filter and to wash. Moreover, the purity of the precipitate is controlled by the tremendously large surface area of the precipitate and by the localized electrical character of the colloidal surface.

The stability of colloidal solutions and suspensions is governed by two major forces, one of attraction between the particles (van der Waals) and one of repulsion (electrical double layer) (Salutsky, 1959, p. 745). This repulsive force is a result of the adsorptive capacity of the colloidal particles for their own ions. For instance, when silver chloride is precipitated in the presence of excess silver ions, the particles adsorb silver ions and become positively charged. Then counter-ions of opposite charge (in this case, nitrate ions) tend to adsorb to the particles to form a second electrical layer, as illustrated in Figure 14.5.

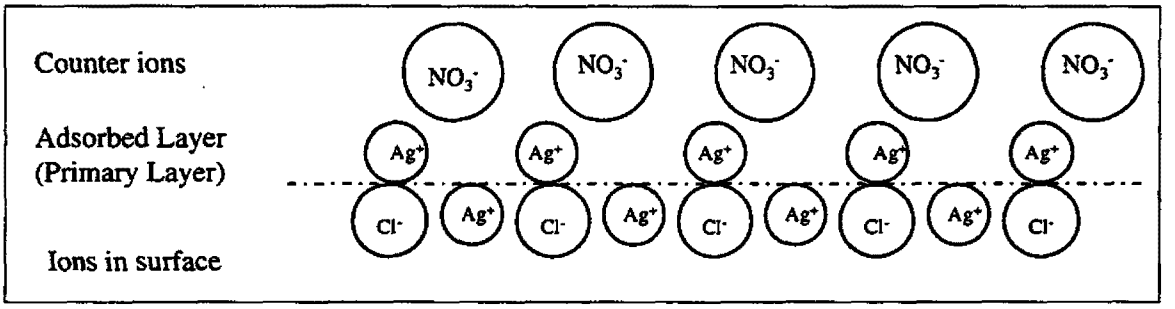


FIGURE 14.5 — The electrical double layer: A schematic representation of adsorption of nitrate counter-ions onto a primary adsorbed layer of silver ions at the surface of a silver chloride crystal (Peters et al., 1974).

In a similar fashion, in the presence of a slight excess of alkali chloride, the silver chloride particles would adsorb chloride ions and become negatively charged. Therefore, precipitates brought down in the presence of an excess of one of the lattice ions tend to be contaminated with ions of the opposite charge. Moreover, because all of the particles have the same charge, they repel each other. If these repulsive forces exceed the attractive van der Waals' forces, a stable colloid results, and the tightness with which the counter-ions are held in and with the water layer,

or the completeness with which they cover the primary adsorbed ion layer, determines the stability of the colloid.

Such adsorption of ions upon the surface of solids in solution is largely, but not entirely, based upon electrical attraction, otherwise adsorption would not be selective. Recall that there are four other factors, in addition to magnitude of charge, that affect the preferential adsorption by a colloid (see *Surface Adsorption* in Section 14.8.4.1, "Coprecipitation Process").

- The Paneth-Fajans-Hahn Law dictates that when two or more types of ions are available for adsorption, the ion that forms the least soluble compound with one of the lattice ions will be adsorbed preferentially.

- The ion present in the greater concentration will be adsorbed preferentially.

- Ions with a large radius will be adsorbed more readily than ions with a smaller radius because the larger ion is less hydrated by the solution and not as attracted to the solution phase.

- The ion that is closer to the same size as the lattice ion will be adsorbed preferentially. For example, radium ions are adsorbed tightly onto barium sulfate, but not onto calcium sulfate; radium ions are close in size to barium ions, but are much larger than calcium ions.

If an excess of electrolyte is added to the colloidal solution, the electrical double layer is destroyed and the particles can agglomerate to form larger particles that can settle to the bottom of the container, a process known as *flocculation* (or *coagulation*). For example, Smith et al. (1995) used polyethylene glycol to remove colloidal silica from a dissolved-soil solution before the addition of the sample to an ion-exchange resin. Alternatively, the process whereby coagulated particles pass back into the colloidal state is known as *deflocculation*, (or *peptization*). Special precautions should be taken during the washing of coagulated precipitates to assure that deflocculation does not occur. When coagulation is accomplished through charge neutralization, deflocculation would occur if the precipitate was washed with water. A solution containing a volatile electrolyte such as nitric acid should be used instead.

There are two types of colloidal solutions (Salutsky, 1959, p. 744):

- *Hydrophobic colloids* show little or no attraction for water. These solutions have a low viscosity, can be easily flocculated by the addition of an appropriate electrolyte, and yield precipitates that are readily filterable.

- *Hydrophilic colloids* have a high affinity for water and are often highly viscous. They are more difficult to flocculate than hydrophobic colloids, and relatively large amounts of electrolytes are necessary to cause precipitation. The flocculate keeps water strongly adsorbed and tends to form jellylike masses that are difficult to filter.

Colloidal precipitations can be a useful separation technique. Because of their great adsorption capacity, colloidal precipitates are excellent *scavengers* (*collectors*) for concentrating trace substances (Salutsky, 1959, p. 747). Unspecific carriers such as manganese dioxide, sulfides and hydrated oxides are frequently used as scavengers. For example, protactinium can be efficiently scavenged and concentrated on manganese dioxide that is precipitated by adding a manganous salt to a solution containing permanganate. Ferric hydroxide is commonly used to scavenge cations (Section 14.8.4.4, "Coprecipitation Methods"). Moreover, scavenging precipitations can sometimes be used to remove interferences. For example, a radionuclide that is capable of existing in two oxidation states can be effectively purified by precipitation in one oxidation state, followed by scavenging precipitations for impurities, while the element of interest is in another oxidation state. A useful procedure for cerium purification involves repeated cycles of ceric iodate precipitation, reduction to Ce^{+3}, zirconium iodate ($ZrIO_3$) precipitation to remove impurities (with Ce^{+3} staying in solution), and reoxidation to Ce^{+4}.

14.8.6 Filterability of Precipitates

The physical nature of a precipitate not only affects the purity of the precipitate, but also the filterability of the precipitate. Large, well-formed crystals are desirable because they tend to contain fewer impurities, and are also easier to filter and wash. Many coagulated colloidal precipitates, such as hydrous oxides or sulfides, tend to form slimy aggregates and to clog the filter during filtration. There are several approaches that can be taken to improve the physical form of the precipitate (Salutsky, 1959, pp. 758-761):

- A trace quantity of a hydrophilic colloid can be added to produce complete and rapid flocculation. For example, gelatin has been used as a *sensitizer* in the precipitation of zinc sulfide, hydrous silica, and various other hydrous oxides, as well-coagulated, filterable precipitates (Salutsky, 1959, p. 759).

- The slow precipitation techniques described in Section 14.8.3.2, "Factors Affecting Precipitation," can be used to produce good precipitates.

- Aging the precipitate can result in a precipitate more amenable to filtration. During *aging*, small particles with a larger solubility go into solution, and larger particles grow at the cost of

the smaller ones (see "Digestion" under Section 14.8.3.2, "Factors Affecting Precipitation"). Ostwald ripening results in a decrease in the number of particles and, therefore, a decrease in surface area. The speed of aging generally increases with temperature and with the increasing solubility of the precipitate in the aging media. Shaking can sometimes promote aging, perhaps by allowing particles to come into contact and to cement together.

Table 14.15 summarizes general properties of common filters used in analytical procedures.

TABLE 14.15 — General properties of common filter papers [1]

Whatman Grade	Particle Retention (μm)	Porosity	Ash (%)	Filter speed	Applications
Qualitative filter papers					
1	> 11	Medium	0.06	Medium-fast	Medium crystalline precipitates. A general purpose filter used in routine laboratory applications, air pollution monitoring, and soil chemical assays.
2	> 8	Medium-fine	0.06	Medium	Crystalline precipitates. More retentive and adsorbent than Grade 1, but with increased filtering time.
3	> 6	Medium-fine	0.06	Medium	Double the thickness of Grade 1 for high precipitate capacity and increased wet strength. Suitable for suction filtration.
4	> 20-25	Coarse	0.06	Fast	Coarse and gelatinous precipitates. Used in air pollution monitoring and for routine cleanup of biological fluids.
5	> 2.5	Fine	0.06	Slow	Fine crystalline precipitates. Most retentive of the series, and is useful for clarifying cloudy suspensions and water analysis.
6	> 3	Fine	0.2	Slow	Fine crystalline precipitates. Twice as fast as Grade 5. Often specified in boiler water analyses.
Quantitative – ashless					
40	> 8	Medium	0.010	Medium	Medium crystalline precipitates: calcium oxalate, well-digested barium. Widely used, general purpose.
41	> 20-25	Coarse	0.010	fast	Gelatinous precipitates and coarse particles: iron and aluminum hydroxides. Also used in quantitative air analyses.
42	> 2.5	Medium	0.010	Slow	Highly retentive for fine particles. The laboratory standard for critical gravimetric analysis.

Whatman Grade	Particle Retention (µm)	Porosity	Ash (%)	Filter speed	Applications
43	> 16	Medium	0.010	Medium-fast	Medium crystalline precipitates. Foodstuff and soil analyses, particle collection in air pollution monitoring by XRF.
44	> 3	Fine	0.010	Slow	Fine crystalline precipitates. Somewhat thinner and faster than Grade 42.
Quantitative – hardened low ash					
50	> 2.7	Fine	0.025	Slow	Hardened papers are designed for use in Buchner funnels, possess great wet strength and lintless surfaces, and will withstand scraping. Grade 50: fine crystalline precipitates. Grade 52: crystalline precipitates, general purpose filtration. Grade 54: gelatinous precipitates and coarse particles.
52	> 7	Medium	0.025	Medium	
54	> 20-25	Coarse	0.025	Fast	
Quantitative – hardened ashless					
540	> 8	Medium	0.008	Medium	Crystalline precipitates. Gravimetric analysis of metals in acid/alkali solutions. Collecting hydroxides after precipitation from strong alkali solutions.
541	> 20-25	Coarse	0.008	Fast	Coarse gelatinous precipitates. Used for strongly acidic or alkaline conditions.
542	> 2.7	Fine	0.008	Slow	Fine crystalline precipitates from under demanding acidic/alkali conditions.

(1) Fisher (2000-01)

14.8.7 Advantages and Disadvantages of Precipitation and Coprecipitation

Advantages

- Provides the only practical method of separation or concentration in some cases.
- Can be highly selective and virtually quantitative.
- High degree of concentration is possible.
- Provides a large range of scale (mg to industrial).
- Convenient, simple process.
- Carrier can be removed and procedure continued with tracer amounts of material (e.g., carrier iron separated by solvent extraction).

Disadvantages

- Can be time consuming to digest, filter, and/or wash the precipitate.
- Precipitate can be contaminated by carrying of ions or postprecipitation.
- Sarge amounts of carrier might interfere with subsequent separation procedures.
- Coprecipitating agent might contain isotopic impurities of the analyte radionuclide.
- Scavenger precipitates are not as selective and are more sensitive to changes in separation procedures.

14.9 Carriers and Tracers

14.9.1 Introduction

Radiochemical analysis frequently requires the radiochemist to separate and determine radionuclides that are present at extremely small quantities. The amount can be in the picomole range or less, at concentrations in the order of 10^{-15} to 10^{-11} molar. Analysis of radionuclides using counting techniques, such as alpha spectrometry, liquid scintillation, proportional counting, or gamma spectrometry, allows activities of radionuclides of 10,000 disintegrations per minute (dpm) to be determined easily, even though the number of atoms (and mass percent) of these materials is vanishingly small. Table 14.16 identifies the number of atoms and mass present in several radionuclides, based on an activity of 500 dpm.

TABLE 14.16 — Atoms and mass of select radionuclides equivalent to 500 dpm(1)

Radionuclide	Half-life	Number of Atoms	Mass (g)
Radium-226	1590 y	6.0×10^{11}	2.3×10^{-10}
Polonium-210	140 d	1.5×10^{8}	5.0×10^{-14}
Lead-212	10.6 h	4.5×10^{5}	1.6×10^{-16}
Thallium-208	3.1m	2.3×10^{3}	8.0×10^{-19}

(1) Based on Wahl and Bonner, 1951, p. 102

Considering the minute masses of these analytes and their subsequently low concentration in solution, it is obvious why conventional techniques of analysis, such as gravimetry, spectrophotometry, titrimetry, and electrochemistry, cannot be used for their quantitation. However, it is not immediately obvious why these small quantities might present other analytical difficulties. As described below, the behavior of such small quantities of materials can be seriously affected by macro constituents in an analytical mixture in a way that may be unexpected chemically.

14.9.2 Carriers

The key to radiochemical analysis of samples with multiple radionuclides is effective separation of the different analytes. Separations are most easily accomplished when performed on a macro scale. As described above, however, the analytes are frequently at levels that challenge the analyst and the conventional methods to perform the separations. The use of a material that is different in isotopic make-up to the analyte and that raises the effective concentration of the material to the macro level is referred to as a *carrier*. In many cases, the carrier is a non-radioactive isotope of the analyte. Some carriers are stable isotopes of chemically similar elements.

A distinction exists between traditional and radiochemical analyses when referring to macro amounts. Generally, carriers are present in quantities from a few tenths to several hundred milligrams of material during the progress of the radiochemical separation.

14.9.2.1 Isotopic Carriers

An isotopic carrier is usually a stable isotope of the analyte. Stable strontium (consisting of naturally occurring ^{84}Sr, ^{86}Sr, ^{87}Sr, and ^{88}Sr) is frequently used as the carrier in the analysis of ^{89}Sr and ^{90}Sr. Regardless of the stability of the isotope, the number of protons in the nucleus ultimately governs the chemical properties of the isotope. Thus, all nuclei that have 38 protons are strontium and react as strontium classically does.

The purpose of adding a carrier is to raise the chemical concentration of the analyte to the point where it can be separated using conventional techniques, but for the carrier to perform properly, it must have the same oxidation state and chemical form as the analyte. It is important then to add the carrier to the sample as early as possible in chemical process. For example, in the determination of ^{131}I in milk, the radioiodine might be present as I^{-1}, IO_3^{-1}, CH_3I, or I_2. The analyst should assume that all states are present, and treat the sample so that all atoms are brought to a common oxidation state and chemical form during some step in the procedure, before any separation takes place. If the final step is precipitation of AgI and the carrier is in the IO_3^{-1} form, no precipitate will form since $AgIO_3$ that forms when Ag^{+1} is added is relatively soluble compared to AgI. Furthermore, if separations of other radioisotopes are performed before this step, there is the possibility that quantities of the radioiodine could be trapped in the precipitate with other separated analytes. When concentrations of these materials are very small, even small losses are significant. The carrier also functions to prevent losses of the analyte during the separation of other radionuclides or interfering macro-contaminants. This is another reason that it is essential to add the carrier prior to any chemical treatment of the sample.

The laws of equilibrium for precipitation, distillation, complexation, and oxidation-reduction will apply to the entire chemical form of analyte in solution, both carrier and radioisotope. If, for example, 99.995 percent of all strontium is determined to be precipitated during a radiochemical procedure, then the amount of stable strontium remaining in solution will be 0.005 percent, which means that 0.005 percent of the radiostrontium still remains in the solution as well. Losses such as this occur during any chemical process. Frequently then, carriers are used in radiochemical analyses not only to raise the chemical concentration of the element, but also to determine the yield of the process. In order to determine the exact amount of radionuclide that was originally present in the sample, the yield (sometimes called the recovery) of the radionuclide collected at the end of the procedure should be known. However, since the amount of analyte at the start of

the procedure is the unknown, the yield should be determined by an alternate method. The mass of the radioanalyte is insignificant in comparison to the carrier, and measuring the yield of the carrier (gravimetrically, for example) will allow the calculation of the yield of the analyte.

14.9.2.2 Nonisotopic Carriers

Non-isotopic carriers are materials that are similar in chemical properties to the analyte being separated, but do not have the same number of protons in their nucleus. Usually these carriers will be elements in the same family in the periodic table. In the classical separation of radium by the Curies, the slight difference in solubility of radium chloride versus barium chloride allowed the tedious fractional crystallization of radium chloride to take place (Hampel, 1968, p. 586). When barium is present in macro-quantities and the radium in femtogram quantities, however, the two may be easily precipitated together as a sulfate.

For several elements, non-isotopic carriers are chosen from a different family of elements, but they have the same ionic charge or similar crystalline morphology as the analyte. Lanthanum and neodymium as +3 ions are frequently used as nonisotopic carriers for U(IV) and Pu(IV) in their final separation as insoluble fluorides by the process of coprecipitation (Metz and Waterbury, 1962, p. 254) (see also Section 14.8, "Precipitation and Coprecipitation"). The chemical form of the uranium and plutonium is particularly important for this process; the +4 oxidation state will coprecipitate, but the +6 in the MO_2^{+2} form, will not. Uranium(IV) is present in solution as UO_2^{+2} and, therefore, will not be coprecipitated with lanthanum fluoride. However, it is very important to note that even though the precipitation of LaF_3 may be quantitative (i.e., >99.995 percent may be precipitated), there is no measure of how much uranium will also be coprecipitated. Since uranium and plutonium are not chemically equivalent, the laws of solubility product constant for lanthanum cannot be applied to uranium. For these types of processes, separate methods should be used to determine the chemical yield of the process.

For alpha counting rare earths, fluorides (such as NdF_3) are frequently used to coprecipitate elements (Hindman, 1983 and 1986; Sill and Williams, 1981).

Another group of non-isotopic carriers can be described as general scavengers. Substances with high surface areas, or the ability to occlude contaminants in their floc, can be used to effect gross separation of all radionuclides from macro quantities of interfering ions. Ferric hydroxide, manganese dioxide (MnO_2) and sulfides (MnS), and hydrated oxides [$Mn(OH)_x$] are examples of these nonspecific carriers that have been used in many radiochemical separations to eliminate gross quantities of interfering substances.

14.9.2.3 Common Carriers

Carriers for specific analytes are discussed below.

Alkaline Earths

STRONTIUM AND BARIUM. Carrier-free strontium (Sr^{2}) and barium (Ba^{+2}) will coprecipitate with ferric hydroxide [$Fe(OH)_3$], while calcium (Ca^{+2}) exhibits the opposite behavior and does not coprecipitate with ferric hydroxide. Lead sulfate ($PbSO_4$) will also carry strontium and barium.

Frequently, inactive strontium and barium are used as carriers for the radionuclides in order to facilitate separation from other matrix constituents and from calcium. The precipitates used most frequently in radiochemical procedures are the chromates (CrO_4^{-2}), nitrates (NO_3^{-1}), oxalates ($C_2O_4^{-2}$), sulfates (SO_4^{-2}), and barium chloride ($BaCl_2$). Several different methods of separation are identified here:

- Chromate precipitation is used in the classical separation of the alkaline earths. Barium chromate ($BaCrO_4$) is precipitated from a hot solution buffered to a pH of 4 to minimize strontium and calcium contamination of the barium precipitate. Ammonium ion (NH_4^{+1}) is then added to the solution, and strontium chromate ($SrCrO_4$) is precipitated.

- Barium and strontium can be separated from calcium as the nitrates. Fuming nitric acid is used to increase the nitric acid concentration to 60 percent, conditions at which barium and strontium nitrate [$Ba(NO_3)_2$ and $Sr(NO_3)_2$] precipitate and calcium does not.

- Oxalate precipitation does not separate one alkaline earth from another, but it is usually used to produce a weighable and reproducible form suitable for radioassay. The precipitation is accomplished from a basic solution with ammonium oxalate [$(NH_4)_2C_2O_4$].

- Barium sulfate ($BaSO_4$) precipitation is generally not used in separation procedures. It is more common as a final step to produce a precipitate that can be readily dried, weighed, and mounted for counting. Barium is readily precipitated by slowly adding dilute sulfuric acid (H_2SO_4) to a hot barium solution and digesting the precipitate. For the precipitation of strontium or calcium sulfate ($SrSO_4$ and $CaSO_4$), a reagent such as alcohol should be added to lower the solubility, and the precipitant must be coagulated by heat.

- Insolubility of barium chloride ($BaCl_2$) in strong hydrochloric acid solution (HCl) is the basis of the method to separate barium from calcium, strontium, and other elements. The

precipitation is performed either by adding an ether-hydrochloric acid solution or by bubbling dry hydrogen chloride gas into the aqueous solution.

RADIUM. Radium (Ra) yields the same types of insoluble compounds as barium: sulfates, chromates, carbonates (CO_3^{-2}), phosphates (PO_4^{-3}), oxalates, and sulfites (SO_3^{-2}). Hence, radium coprecipitates with all barium compounds and, to a lesser extent, with most strontium and lead compounds. Barium sulfate and barium chromate are most frequently used to carry radium. Other compounds that are good carriers for radium include ferric hydroxide when precipitated at moderately high pH with sodium hydroxide (NaOH), barium chloride when precipitated from a cold mixed solvent of water and alcohol saturated with hydrochloric acid, barium iodate ($BaIO_3$) and various insoluble phosphates, fluorides (F^{-1}) and oxalates (e.g., thorium phosphate [$Th_3(PO_4)$], lanthanum fluoride (LaF_3), and thorium oxalate [$Th(C_2O_4)$].

Rare Earths, Scandium, Yttrium, and Actinium

Ferric hydroxide and calcium oxalate (CaC_2O_4) will coprecipitate carrier-free rare earths without difficulty.

The rare earths will coprecipitate one with another in almost all of their reactions; one rare earth can always be used to coprecipitate another. The rare earth hydroxides, fluorides, oxalates, and 8-hydroxyquinolates in ammoniacal solution are insoluble. Conversely, the rare earth hydroxides will carry a number of elements that are insoluble in basic solution; the rare earth oxalate will coprecipitate calcium; and the rare earth fluorides tend to carry barium and zirconium (Zr). In the absence of macro quantities of rare earths, actinium will carry on barium sulfate and lead sulfate ($PbSO_4$).

Lead

Ferric hydroxide and aluminum hydroxide [$Al(OH)_3$] carry lead very effectively from ammonium solutions under a variety of conditions. Lead is carried by barium or radium chloride, but not carried by barium or radium bromide ($BaBr_2$ or $RaBr_2$). This behavior has been used to separate radiolead isotopes from radium salts. Lead is also carried by barium carbonate ($BaCO_3$), barium sulfate, radium sulfate, radium chloride, lanthanum carbonate [$La_2(CO)_3$], barium chloride, and silver chromate (Ag_2CrO_4). Calcium sulfate in the presence of alcohol has also been used to coprecipitate lead.

Polonium

Trace quantities of polonium (Po) are carried almost quantitatively by bismuth hydroxide [$Bi(OH)_3$] from ammoniacal solution. Ferric, lanthanum, and aluminum hydroxides have also been used as carriers for polonium in alkaline solutions. Colloidal platinum and coagulated silver hydroxide (AgOH) and ferric hydroxide sols have been used to carry polonium. Because of the high oxidation state of polonium, it is susceptible to being a contaminant in almost any precipitate. Removal of polonium by electrodeposition on nickel metal is recommended prior to final precipitation for any gross counting technique (proportional counting and liquid scintillation, for example).

Actinides

THORIUM. Thorium (Th) will coprecipitate with ferric, lanthanum [$La(OH)_3$], and zirconium hydroxide [$Zr(OH)_4$]. These hydroxide carriers are nonspecific, and therefore, will only remove thorium from a simple group of contaminants or as a group separation. The ferric hydroxide precipitation is best carried out at pH 5.5-6.

Thorium will coprecipitate quantitatively with lanthanum fluoride from strongly acidic solutions, providing an effective means to remove small quantities of thorium from uranium solutions. However, the rare earths will also carry quantitatively, and zirconium and barium radioisotopes will carry unless macro quantities of these elements are added as holdback carriers (see Section 14.9.2.4, "Holdback Carriers").

Precipitation of thorium with barium sulfate is possible from strongly acidic solutions containing high concentrations of alkali metal sulfates; however, this coprecipitation is nonspecific. Other actinides, lead, strontium, rare earths, bismuth, scandium (Sc), and yttrium will also carry.

Coprecipitation of thorium on hydrogen hypophosphate (HPO_3^{-2}) or phosphate carriers can be performed from rather strongly acidic solutions. Zirconium phosphate [$Zr_3(PO_4)_4$] serves as a good carrier for trace levels of thorium. Moreover, thorium also will carry quantitatively on zirconium iodate from a strongly acidic solution. If coprecipitation is performed from a strongly acidic solution and the precipitate is washed with a solution containing iodate, the rare earths and actinium are eliminated. Ce^{+4} must be reduced to Ce^{+3} before precipitation so that it does not carry.

PROTACTINIUM. Protactinium will be carried quantitatively on hydroxide, carbonate, or phosphate precipitates of tantalum (Ta), zirconium, niobium (Nb), hafnium (Hf), and titanium

(Ti). It is also carried by adsorption onto flocculent precipitates of calcium hydroxide [$Ca(OH)_2$)] or ferric hydroxide, and it is carried by manganese dioxide, which is produced by addition of potassium permanganate ($KMnO_4$) to a dilute nitric acid (HNO_3) solution containing manganese nitrate. However, titanium and zirconium are also carried under these conditions.

URANIUM. Trace concentrations of uranium can be coprecipitated with any of the common insoluble hydroxides. When coprecipitating U(VI) with hydroxides at pH 6-7, the ammonium used must be free of carbonate or some of the uranium will remain in solution as the stable anionic carbonate complex. Hydroxide precipitation is nonspecific, and many other metals will carry with the uranium.

Uranium(IV) can be coprecipitated as the fluoride or phosphate [UF_4 or $U_3(PO_4)_4$] from relatively strong acid media; however, U(VI) phosphate [$(UO_2)_3(PO_4)_2$] is precipitated only from very weak acid solutions (pH 5-6) by the addition of carbonate-free ammonium. The rare earths, and other metals can also coprecipitate under these conditions.

In general, U^{+4} should behave similarly to Pu^{+4} and Np^{+4}, and should be carried by lanthanum fluoride, ceric and zirconium iodates [$Ce(IO_4)_3$ and $Zr(IO_4)_4$], cerium and thorium oxalates [$Ce_2(PO_4)_3$], barium sulfate, zirconium phosphate [$Ce_2(PO_4)_3$], and bismuth arsenate ($BiAsO_4$). However, U(VI) does not carry with these agents as long as the concentration of either carrier or that of uranium is not too high.

PLUTONIUM AND NEPTUNIUM. Classically, plutonium (Pu) and neptunium (Np) in their ter- and tetravalent oxidation states have been coprecipitated with lanthanum fluoride in the method most widely used for the isolation of femtograms of plutonium. However, large amounts of aluminum interfere with coprecipitation of plutonium, and other insoluble fluorides, such as the rare earths, calcium, and U^{+4}, coprecipitate.

AMERICIUM AND CURIUM. Bismuth phosphate ($BiPO_4$), which historically has been used to precipitate plutonium, will also carry americium and curium from 0.1-0.3 M nitric acid. Impurities such as calcium and magnesium are not carried under these conditions.

Lanthanum fluoride provides a convenient carrier for Am^{+3} and Cm^{+3}. A lanthanum fluoride precipitation is not totally specific, but it can provide a preliminary isolation from the bulk of the fission products and uranium. Additionally, a lanthanum fluoride precipitation can be used to separate americium from curium. Am^{+3} is oxidized to Am(V) in dilute acid with persulfate, and fluoride is added to precipitate Cm^{+3} on lanthanum fluoride.

14.9.2.4 Holdback Carriers

It is often necessary to add holdback carriers to analytical mixtures to prevent unwanted radionuclides from being carried in a chemical process. Coprecipitation of a radionuclide with ferric hydroxide carries other ions in addition to the analyte, because of its tendency to adsorb other ions and occlude them in its crystal matrix. The addition of a holdback carrier, a highly-charged ion, such as Co^{+3}, represses counter-ion exchange and adsorption to minimize the attraction of foreign ions. The amount of a given substance adsorbed onto a precipitate depends on its ability to compete with other ions in solution. Therefore, ions capable of displacing the radionuclide ions (the hold-back carrier) are added to prohibit the coprecipitation of the radionuclide. Highly charged ions, chemical homologs, and ions isotopic with the radionuclide are among the most efficient holdback carriers. Hence, the addition of inactive strontium makes it possible to precipitate radiochemically pure radiobarium as the nitrate or chloride in the presence of radiostrontium. Actinium and the rare earth elements can be separated from zirconium and radium by lanthanum fluoride coprecipitation with the addition of zirconium and barium holdback carriers. Holdback carriers are used in other processes as well. The extraction of lutetium from water employs neodymium ions (Nd^{+3}) to avoid adsorption loses (Choppin et al., 1995, p. 262).

14.9.2.5 Yield (Recovery) of Isotopic Carriers

The use of an isotopic carrier to determine the chemical yield of the analyte is a critical step in the plan of a radiochemical analysis. The analytical method being used to determine the final amount of carrier will govern the method of separation. If a gravimetric method is to be used for the final yield determination, the precipitate must have all the characteristics that would be used for macro gravimetric analysis—easily dried, definite stoichiometry, non-hygroscopic, and the like.

Similarly, the reagent used as source of carrier at the beginning of the analysis must be of primary-standard quality to ensure that the initial mass of carrier added can be determined very accurately. For a gravimetric yield determination, the equation would be the following:

$$\text{Percent Yield} = \frac{\text{(mass of carrier in final separation step)}}{\text{(mass of carrier added)}} \times 100\%$$

It should be recognized that the element of interest is the only quantity used in this formula. For example, if strontium nitrate is used as the primary standard and strontium sulfate is the final

precipitate, both masses should be corrected, using a gravimetric factor, so that only the mass of strontium is used in the equation in both the numerator and denominator.

Other methods to determine the yield of the carrier include atomic absorption spectrometry, ultraviolet/visible spectrometry, titrimetry, and potentiometry.

14.9.3 Tracers

The term *tracer* was classically used to express the concentration of any pure radionuclide in solution that had a mass too small to be measured by an analytical balance (<0.0001 to 0.00001 g). More recently, the definition of a tracer has become more pragmatic. The current definition of a tracer is a known quantity of a radioisotope that is added to a solution of a chemically equivalent radioisotope of unknown concentration so that the yield of the chemical separation can be monitored. In general, a tracer is not a carrier, and a carrier is not a tracer.

The analysis of ^{241}Am in an environmental sample provides an example of a radioisotope employed in a manner consistent with the recent use of the term *tracer*. In the analytical procedure, no stable isotope of americium exists to act as a carrier. Femtogram quantities of ^{243}Am can be produced, however, with accurately known activities. If a known quantity of ^{243}Am in solution is added to the unknown sample containing ^{241}Am at the beginning of the separation procedure, and if the resulting activity of ^{243}Am can be determined at the end of the procedure, then the yield of ^{241}Am can be determined accurately for the process. ^{243}Am added to the sample in this example is used as a tracer. A measurable mass of this element was not used, but a known activity was added through addition of the solution. During the course of the radiochemical separation, lanthanides may have been used to help carry the americium through analysis. However, they are not used to determine the yield in this example and would be considered, therefore, a non-isotopic carrier.

When using a tracer in an analytical method, it is important to consider the availability of a suitable isotope, its chemical form, its behavior in the system, the amount of activity required, the form in which it should be counted, and any health hazards associated with it (McMillan, 1975, p. 298).

Perhaps the most important property of the tracer is its half-life. It is preferable to select an isotope with a half-life that is long compared to the duration of the experiment. By doing so, one avoids the problems of having to handle high levels of activity at the beginning of the experiment and of having to make large decay corrections.

Purity of the tracer is of critical importance. Radionuclide and radiochemical impurities are the two principal types of impurities encountered. Radionuclide impurity refers to the presence of radionuclides other than those desired. For instance, it is very difficult to obtain ^{236}Pu tracer that does not contain a very small quantity of ^{239}Pu. This impurity should be taken into account when calculating the ^{239}Pu activity levels of samples. Radiochemical impurity refers to the nuclide of interest being in an undesired chemical form. This type of impurity has its largest effects in organic tracer studies, where the presence of a tracer in the correct chemical form is essential. For example, the presence of ^{32}P-labeled pyrophosphate in an orthophosphate tracer could lead to erroneous results in an orthophosphate tracer study.

Tracer solutions can also contain other forms of radiochemical impurities. Many tracers are actinides or other isotopes that have progeny that are radioactive. Tracer solutions are purchased with known specific activities for the isotopes listed in the solutions. However, from the time of production of the tracer, ingrowth of progeny radioisotopes occurs. ^{236}Pu is used as a tracer for ^{239}Pu and ^{240}Pu analysis, for example. ^{236}Pu has a half-life of 2.9 years and decays to ^{232}U, which has a half-life of 72 years. After solutions of ^{236}Pu have been stored for about three years, half of the radionuclide will be converted to ^{232}U. If the solution is then used as a tracer in a procedure for analysis of uranium and plutonium in soil, erroneously high results would be produced for the content of uranium if a gross-counting technique is used. Thus, it is important to consider chemical purification of a tracer solution prior to use to remove unwanted radioactive progeny.

Tracer analysis is very dependent upon the identical behavior of the tracer and the analyte. Therefore, tracers should be added to the system as early as possible, and complete isotopic exchange should be ensured as discussed previously (see Section 14.10, "Radiochemical Equilibrium"). Obvious difficulties arise when a tracer is added to a solid sample, especially if the sample is subdivided. Unless complete dissolution and isotopic exchange is ensured, results should be interpreted carefully.

Isotopes selected for tracer work should be capable of being easily measured. Gamma-emitting isotopes are ideal because they can easily be detected by gamma spectroscopy without being separated from other matrix constituents. Alpha- and beta-emitting tracers require separation before counting. Some common tracers are listed below:

- ^{85}Sr has a 514 KeV gamma ray that can be used to monitor the behavior of strontium in a system, or for yield determination in a $^{89}Sr/^{90}Sr$ procedure, as long as the gamma is accounted for in the beta-counting technique.

- ^{99m}Tc with a half-life of 6.02 h and a 143 KeV gamma ray is sometimes used as a yield monitor for ^{99}Tc determinations. Samples are counted immediately to determine the chemical recovery, then the ^{99m}Tc is allowed to decay before analysis of the ^{99}Tc.

- ^{152}Eu and ^{145}Sm are frequently used in the development of a new method to estimate the behavior of the +3 actinides and lanthanides.

- ^{3}H, ^{14}C, ^{32}P, and ^{36}Cl are frequently used in biological studies. In some of these studies, the radionuclide is covalently bonded to a molecule. As a result, the chemical behavior of the radionuclide will follow that of the molecule, not the element.

- ^{229}Th is used for Th determinations, both in alpha spectroscopy and inductively coupled plasma-mass spectroscopy (ICP-MS).

- ^{232}U is commonly used as a tracer in alpha spectroscopy, whereas ^{236}U is used for ICP-MS determinations. It should be noted that ^{232}U decays to ^{228}Th and therefore needs to be taken into account if determining Th isotopes in the same sample.

- ^{242}Pu and ^{236}Pu are both used as tracers in Pu analyses. However, ^{236}Pu decays to ^{232}U, which needs to be taken into account when analyzing both Pu and U in the same sample aliquant.

- ^{243}Am is employed in the analysis of ^{241}Am and Cm by alpha spectroscopy. It is assumed that Am and Cm are displaying similar chemical behavior.

14.9.3.1 Characteristics of Tracers

The behavior of tracers is often different from that of elements in normal concentrations. The chemical form of a radionuclide predominant at normal concentrations, for example, might not be the primary form at tracer concentrations. Alternatively, a shift in the equilibrium that is partly responsible for a radionuclide's chemical behavior might increase or reduce its concentration as a result of the low tracer concentration. Hydrolysis reactions are influenced particularly by changes in concentration because water is one of the species in the equilibrium. For example, hydrolysis of the uranyl ion is represented by (Choppin et al., 1995, p.243):

$$m \cdot UO_2^{+2} + p \cdot H_2O \rightarrow (UO_2)_m(OH)_p^{2m-p} + p \cdot H^{+1}$$

At tracer quantities, the equilibrium will shift to the left as the amount of the uranyl ion decreases. At 10^{-3} molar (pH 6), the uranyl ion is 50 percent polymerized; at 10^{-6} molar, there is negligible polymerization.

Interactions of radionuclides with impurities present special problems at low concentration. Difficulties include adsorption onto impurities such as dust, silica, or colloidal or suspended material, or adsorption onto the walls of the container. Generally, 10^{-8} to 10^{-7} moles are needed to cover a container's walls; but at tracer concentrations, much less is present (Choppin et al., 1995, p. 242). Adsorption depends on (see *Surface Adsorption* within Section 14.8.4.1, "Coprecipitation Processes"):

- *Concentration.* A larger percentage is adsorbed at lower tracer concentrations than at higher concentrations, because a larger surface area is available compared to the amount of tracer present. Dilution with carrier decreases the amount of tracer adsorbed because the carrier is competing for adsorption, and the relative amount of tracer interacting with the walls is much less.

- *Chemical State.* Adsorption increases with charge on the ion.

- *Nature of the Surface Material.* Surfaces that have a negative charge or that contain hydroxyl groups can interact with cations through electrostatic attraction and hydrogen bonding, respectively.

- *pH.* Generally, adsorption decreases with a lower pH (higher hydrogen ion concentration) because the ions interact with negatively-charged surfaces, and hydrogen bonding decreases their ability to interact with metal ions.

All these processes will reduce the quantity of analyte available for radiochemical procedures and, therefore, the yield of a procedure. The amount measured by the detection process will be correspondingly lower, introducing additional error and uncertainty that would go undetected at normal concentrations.

Adsorption can be useful, however. For example, carrier-free yttrium (Y^{+3}) is quantitatively adsorbed onto filter paper from basic strontium solutions at concentrations at which yttrium hydroxide, $Y(OH)_3$, will not precipitate. Also, carrier-free niobium (Nb) has been adsorbed on glass fiber filters for a fast specific separation technique (Friedlander et al., 1981, p. 296).

Specific behavior characteristics of compounds in separation techniques are further described below. Additional discussion can also be found in the respective sections found earlier in this document that describe each separation technique.

14.9.3.2 Coprecipitation

Often, the concentration of tracer is so low that precipitation will not occur in the presence of a counter-ion that, at normal concentrations, would produce an insoluble salt. Under these conditions, carriers are used to coprecipitate the tracer. (Coprecipitation is described in Section 14.8)

14.9.3.3 Deposition on Nonmetallic Solids

Radionuclides can be deposited onto preformed ionic solids, charcoal, and ion-exchange resins (Wahl and Bonner, 1951, p. 124). The mechanisms of adsorption onto preformed ionic solids are similar to those responsible for coprecipitation: counter-ion exchange and isomorphous exchange (Section 14.8, "Precipitation and Coprecipitation"). Adsorption is favored by a large surface area, charge of the solid and radionuclide, solubility of compound formed between the solid and the radionuclide, and time of contact; however, it depends, to a large extent, on whether or not the radionuclide ion can fit into the crystal lattice of the precipitate. Similarly, adsorption onto charcoal depends on the amount of charcoal and its surface area, time of contact, and nature of the surface, because it can be modified by the presence of other ions or molecules.

Adsorption of radionuclides, with and without carriers (Friedlander et al., 1981, p. 297), onto ion-exchange resins, followed by selective elution, has been developed into a very efficient separation technique (Wahl and Bonner, 1951, p. 145) (see Section 14.6.4, "Ion-Exchange Chromatography"). Friedlander et al. (1981), illustrates this phenomenon:

> "Ion-exchange separations generally work as well with carrier-free tracers as with weighable amounts of ionic species. A remarkable example was the original isolation of mendelevium at the level of a few atoms (p. 298)...The transuranium elements in the solution were ... separated from one another by elution ...through a cation-exchange column" (p. 450).

14.9.3.4 Radiocolloid Formation

At the tracer level, a radionuclide solution is not necessarily truly homogeneous, but can be a microparticle (colloid) of variable size or aggregation (Adolff and Guillaumont, 1993, p. 196). Carrier-free tracers can become colloidal by two mechanisms:

1. Sorption onto a preexisting colloidal impurity (approximately 0.001 μ to 0.5 μ), such as dust, cellulose fibers, glass fragments, organic material, and polymeric metal hydrolysis products (Choppin et al., 1995, p. 243; Adolff and Guillaumont, 1993, p. 196)

2. Polycondensation of a monomeric species consisting of aggregates of 10^3 to 10^7 radioactive atoms (Adolff and Guillaumont, 1993, p. 197)

The presence of radiocolloids in solution can be detected by one or more of the following characteristics of the solution, which is not typical behavior of a true solution (Adolff and Guillaumont, 1993, p. 196):

- The radionuclide can be separated from solution by a physical method such as ultrafiltration or ultracentrifugation.

- The radionuclide does not follow the laws of a true solution when a chemical gradient (diffusion, dialysis, isotopic exchange) or electrical gradient (electrophoresis, electrolysis, electrodialysis) is applied.

- Adsorption on solid surfaces and spontaneous deposition differ from those effects observed for radionuclides in true solution.

- Autoradiography reveals the formation of aggregates of radioactive atoms.

Several factors affect the formation of radiocolloids (Wahl and Bonner, 1951, pp. 145-148):

- *Solubility of the Tracer.* The tendency of the tracer radionuclide to hydrolyze and form an insoluble species with another component of the solution favors radiocolloid formation, while the presence of ligands that form soluble complexes hinders formation; low pH tends to minimize hydrolysis of metallic radionuclides.

- *Foreign Particles.* The presence of foreign particles provides sites for the tracer to adsorb onto their surfaces; solutions containing ultrapure water prepared with micropore filters reduce their presence, although the preparation of water completely free of suspended particles is difficult.

- *Electrolytes.* Electrolytes affect the nature (species) of the tracer ions in solution (see Section 14.10, *Radiochemical Equilibrium*), as well as the charge on both the radiocolloid and the foreign particle from which the colloid might have been derived.

- *Solvent.* Polar and nonpolar solvents can favor the formation of radiocolloids, depending on the specific radiocolloid itself.

- *Time.* The amount of radiocolloidal formation generally increases with the age of solution.

14.9.3.5 Distribution (Partition) Behavior

Distribution (partition) coefficients, which reflect the behavior of solutes during solvent extraction procedures (Section 14.4, "Solvent Extraction"), are virtually independent of concentration down to tracer concentrations (Friedlander et al., 1981, p. 299). Whenever the radioactive substance itself changes into a different form, however, the coefficient naturally changes, affecting the distribution between phases during extraction or any distribution phenomena, such as ion-exchange or gas-liquid chromatography (Section 14.7, "Chromatography"). Several properties of tracer solutions can alter the physical or chemical form of the radionuclide in solution and alter its distribution behavior (Wahl and Bonner, 1951, pp. 149-151):

- Radiocolloid formation might concentrate the radionuclide in the alternate phase or at the interface between the phases.

- Shift in equilibrium during complex-ion formation or hydrolysis reactions can alter the concentration of multiple radionuclide species in solution (Section 14.9.3.1, "Characteristics of Tracers").

14.9.3.6 Vaporization

Radioisotope concentrations that challenge the minimum detectible concentration (MDC) can be vaporized from solid surfaces or solution (Section 14.5, "Volatilization and Distillation"). Most volatilization methods of these trace quantities of radionuclides can be performed without specific carriers, but some nonisotopic carrier gas might be required (Friedlander et al., 1981, p. 300).

Vaporization of these amounts of materials from solid surfaces differs from the usual process of vaporization of macroamounts of material, because the surface of the solid is usually not completely covered with the radionuclide (Wahl and Bonner, 1951, pp. 151-158). Carrier-free radionuclides at the surface are bonded with the surface particles instead of with themselves, and the bonds broken during the process are between the solid and the radioisotope, rather than

between the radioisotope particles themselves. Additionally, the nature of the radioisotope can be altered by small trace quantities of gases such as oxygen and water present in the vacuum. Therefore, the identity of the radionuclide species vaporizing might be uncertain, and the data from the procedure can be hard to interpret. The rate of vaporization of radioisotopes also decreases with time, because the number of radioisotope particles available on the solid surface decreases with time.

Radioisotopes near the MDC and macroquantities of radionuclide solutes should behave very similarly in vaporization experiments from solution, however, because both are present as a small fraction of the solution. They are, therefore, surrounded and bonded to solvent molecules rather than to other solute particles (Wahl and Bonner, 1951, p. 156). The nature of the solvent, the pH, and the presence of electrolytes generally affect the solubility of the solute and its vaporization behavior.

14.9.3.7 Oxidation and Reduction

Some radionuclides exist in only one oxidation state in solution, but others can exist in several stable states (Tables 14.1 and 14.2). If multiple states are possible, it might be difficult to ascertain in which state the radionuclide actually exists because the presence of trace amounts of oxidation or reduction (redox) impurities might convert the radionuclide to a state other than the one in which it was prepared (Wahl and Bonner, 1951, pp. 158-159). Excess redox reagents can often be added to the solution to convert the forms to a fixed ratio and keep the ratio constant during subsequent procedures.

For a redox equilibrium such as:

$$PuO_2^{+2} + 4\ H^{+1} + Hg \rightarrow Pu^{+4} + Hg^{+2} + 2\ H_2O$$

the Nernst equation is used to calculate the redox potential, E, from the standard potential, E^0:

$$E = E^0 - kT\ \ln([Pu^{+4}][Hg^{+2}]/[PuO_2^{+2}][H^{+1}]^4)$$

where k is a constant for the reaction (R/2F, containing the ideal gas constant, R, and Faraday's constant, F) and T is the absolute temperature. Water and metallic mercury (Hg) do not appear in the equation, because their activity is one for a pure substance. Minute concentrations of ions in solution exhibit the same redox potential as macroquantities of ions because, E depends on the ratio of ion concentrations and not their total concentration.

Electrolysis of some solutions is used for electrodeposition of a carrier-free metal on an electrode (Choppin et al., 1995, p. 246) or other substance, leaving the impurities in solution (Friedlander et al., 1981, p. 301). The selectivity and efficiency, characteristic of deposition of macro-quantities of ions at a controlled potential, is not observed, however, for these metals. The activity of the ion is not known, even if the concentration is, because the activity coefficient is dependent on the behavior of the mixed electrolytic system. In addition, the concentration of the metal in solution might not be known because losses may occur through adsorption or complexation with impurities. Electrolytic deposits are usually extremely thin—a property that makes them useful for counting measurements (Wahl and Bonner, 1951, p. 162).

Deposition by chemical displacement is sometimes used for the separation of tracer from bulk impurities (Friedlander et al., 1981, p. 301). Polonium and lead spontaneously deposit from a solution of hydrochloric acid onto a nickel disk at 85 °C (Blanchard, 1966). Alpha and beta counting is then used to determine ^{210}Po and ^{210}Pb. The same technique is frequently used in low-level analysis of transuranic elements to remove lead and polonium so that they do not interfere with the subsequent alpha analysis of the elements. Wahl and Bonner (1951, pp. 460-465) contains a helpful table (6F) of electrochemical methods used for the oxidation and reduction of carrier-free tracers.

14.10 Radiochemical Equilibrium

14.10.1 Basic Principles of Equilibrium

Radiochemical analysis is based on the assumption that an element reacts the same chemically, whether or not it is radioactive. This assumption is valid when the element (analyte) and the carrier/tracer are in the same oxidation state, complex, or compound. The atomic weight of most elements is great enough that the difference in atomic weight between the radionuclide of interest and the carrier or tracer will not result in any chemical separation of the isotopes. This assumption might not be valid for the very lightest elements (e.g., H, Li, Be, and B) when mass fractionation or measuring techniques are used.

Most radiochemical procedures involve the addition of one of the following:

- A carrier of natural isotopic composition (i.e., the addition of stable strontium carrier to determine ^{89}Sr/^{90}Sr; EPA, 1980, Method 905.0).

- A stable isotope tracer (i.e., enriched ^{18}O, ^{15}N, and ^{14}C, are frequently used in mass spectroscopy studies).

- A radionuclide tracer (i.e., the addition of a known quantity of ^{236}Pu tracer to determine ^{239}Pu by alpha spectroscopy; DOE, 1990 and 1997, Method Pu-02).

To achieve quantitative yields, there must be complete equilibration (isotopic exchange) between the added isotope and all the analyte species present. In the first example, isotopic exchange of the carrier with the radiostrontium is achieved and a weighable, stoichiometric compound of the carrier and radionuclide are produced. The chemical recovery from the separation technique is determined gravimetrically. Alternatively, a known quantity of an isocesiumtope is used and determined independently by mass analysis, pulse-height analysis, or another counting technique.

Carriers and tracers are added as soon in the sample preparation process as possible, usually after the bulk sample is dried and homogenized, but before sample decomposition to ensure that the chemistry of the carriers or tracers is truly representative of the radioisotope of interest. Thus, losses occurring during sample preparation steps, before decomposition, are not quantified and might not be detected, although losses during these earlier steps are usually minimized. Having the carriers and tracers present during the sample decomposition provides an opportunity to equilibrate the carrier or tracer with the sample so that the carrier, tracer, and analyte are in the identical chemical form. While this can initially appear to be rather easy, in some cases it is extremely difficult. The presence of multiple valence states and the formation of chemical complexes are two conditions that introduce a host of equilibration problems (Section 14.2.2, "Oxidation-Reduction Reactions"; Section 14.2.3, "Common Oxidation States"; and Section 14.2.4, "Oxidation State in Solution"). Crouthamel and Heinrich (1971, pp. 5473-5474) has an excellent discussion of the intricacies and challenges associated with attaining true isotopic exchange:

> "Fortunately, there are many reactions which have high exchange rates. This applies even to many heterogeneous systems, as in the heterogeneous catalysis of certain electron transfer reactions. In 1920, Hevesy, using ThB (^{212}Pb), demonstrated the rapid exchange between active lead nitrate and inactive lead chloride by the recrystallization of lead chloride from the homogeneously mixed salts. The ionization of these salts leads to the chemically identical lead ions, and a rapid isotopic exchange is expected. Similar reversible reactions account for the majority of the rapid exchange reactions observed at ordinary temperatures. Whenever possible, the analyst should conduct the isotope exchange reaction through a known reversible reaction in a homogeneous system. The true homogeneity of a system is not always obvious, particularly when dealing with the very low concentrations of the carrier-free isotopes. Even the usually well-behaved alkali-metal ions in carrier-free solutions will adsorb on the surfaces of their containment

vessels or on colloidal and insoluble material in the solution. This is true especially in the heavier alkali metals, rubidium and cesium. Cesium ions in aqueous solution have been observed to absorb appreciably to the walls of glass vessels when the concentrations were below 10^{-6} g/mL."

The reaction described above can be written as follows:

$$^{212}Pb(NO_3)_2(s) + PbCl_2(s) \rightarrow Pb(NO_3)_2 + {}^{212}PbCl_2$$

Any of the following techniques may be employed to achieve both chemical and isotopic equilibration:

- Careful adding, mixing, stirring, shaking, etc., to assure a homogeneous solution and prevent layering.
- Introducing the carrier or tracer in several different chemical forms or oxidation states, followed by oxidation or reduction to a single state.
- Treating the carrier or tracer and sample initially with strong oxidizing or reducing agents during decomposition (e.g., wet ashing or fusion).
- Carrying out repeated series of oxidation-reduction reactions.
- Requiring that, at some point during the sample decomposition, all the species be together in a clear solution.

Once a true equilibration between carrier or tracer and sample occurs, the radiochemistry problem shifts from one of equilibration to that of separation from other elements, and ultimately a good recovery of the radionuclide of interest.

Crouthamel and Heinrich summarizes the introduction to equilibration (isotopic exchange) (Crouthamel and Heinrich, 1971, pp. 5475-5476):

"Probably the best way to give the reader a feeling for the ways in which isotopic exchange is achieved in practice is to note some specific examples from radiochemical procedures. The elements which show strong tendencies to form radiocolloids in many instances may be stabilized almost quantitatively as a particular complex species and exchange effected. Zirconium, for example, is usually exchanged in strong nitric acid-

hydrofluoric acid solution. In this medium, virtually all the zirconium forms a ZrF_6^{2-} complex. Niobium exchange is usually made in an oxalate or fluoride acid medium. The exchange of ruthenium is accomplished through its maximum oxidation state, Ru(VIII) which can be stabilized in a homogeneous solution and distilled as RuO_4. Exchange may also be achieved by cycling the carrier through oxidation and reduction steps in the presence of the radioactive isotope. An iodine carrier with possible valence states of -1 to +7 is usually cycled through its full oxidation-reduction range to ensure complete exchange. In a large number of cases, isotopic exchange is not a difficult problem; however, the analyst cannot afford to relax his attention to this important step. He must consider in each analysis the possibility of both the slow exchange of certain chemical species in homogenous solution and the possible very slow exchange in heterogeneous systems. In the latter case, this may consist simply of examining the solutions for insoluble matter and taking the necessary steps to either dissolve or filter it and to assay for possible radioactive content."

Also see the discussion of equilibration of specific radionuclides in Section 14.10.9, "Review of Specific Radionuclides."

14.10.2 Oxidation State

Some radionuclides exist in solution in one oxidation state that does not change, regardless of the kind of chemical treatment used for analysis. Cesium (Cs), radium, strontium, tritium (^3H), and thorium are in the +1, +2, +2, +1, and +4 oxidation states, respectively, during all phases of chemical treatment. However, several radionuclides can exist in more than one state, and some are notable for their tendency to exist in multiple states simultaneously, depending on the other components present in the mixture. Among the former are cobalt, iron, iodine, and technetium, and among the latter are americium, plutonium, and uranium. To ensure identical chemical behavior during the analytical procedure, the radionuclide of interest and its carriers and/or tracers in solution must be converted to identical oxidation states. The sample mixture containing the carriers and/or tracer is treated with redox agents to convert each state initially present to the same state, or to a mixture with the same ratio of states. Table 6E in Wahl and Bonner (1951, pp. 450-459) provides a list of traditional agents for the oxidation and reduction of carrier-free tracers that is a useful first guide to the selection of conditions for these radioequilibrium processes.

14.10.3 Hydrolysis

All metal ions (cations) in aqueous solution interact extensively with water, and, to a greater or lesser extent, they exist as solvated cations (Katz et al., 1986, p. 1141):

$$Ra^{+2} + x \cdot H_2O \rightarrow Ra(H_2O)_x^{+2}$$

The more charged the cation, the greater is its interaction with water. Solvated cations, especially those with +4, +3, and small +2 ions, tend to act as acids by hydrolyzing in solution. Simply stated, *hydrolysis* is complexation where the ligand is the hydroxyl ion. To some extent, all metal cations in solution undergo hydrolysis and exist as hydrated species. The hydrolysis reaction for a metal ion is represented simply as (Choppin et al., 1995, p.650):

$$M^{+n} + m \cdot H_2O \rightarrow M(OH)_m^{+(n-m)} + m \cdot H^{+1}$$

Hydrolysis of the ferric ion (Fe^{+3}) is a classical example:

$$Fe^{+3} + H_2O \rightarrow Fe(OH)^{+2} + H^{+1}$$

Considering the hydrated form of the cation, hydrolysis is represented by:

$$M(OH_2)_x^{+n} \rightarrow M(OH_2)_{x-1}(OH)^{(n-1)+} + H^{+1}$$

In the latter equation, the hydrated complex ion associated with the hydroxide ion, is known as the *aquo-hydroxo* species (Birkett et al., 1988, p. 2.7-3). As each equation indicates, hydrolysis increases the acidity of the solution, and the concentration of the hydrogen ion (pH) affects the position of equilibrium. An increase in acidity (increase in H^{+1} concentration; decrease in pH) shifts the position of equilibrium to the left, decreasing hydrolysis, while a decrease in acidity shifts it to the right, increasing hydrolysis. The extent of hydrolysis, therefore, depends on the pH of the solution containing the radionuclide. The extent of hydrolysis is also influenced by the radius and charge of the cation (charge/radius ratio). Generally, a high ratio increases the tendency of a cation to hydrolyze. A ratio that promotes hydrolysis is generally found in small cations with a charge greater than one (Be^{+2}, for example). The thorium cation, Th^{+4}, with a radius three times the size of the beryllium ion but a +4 charge, is hydrolyzed extensively, even at a pH of four (Baes and Mesmer, 1976, p. 158). It is not surprising, therefore, that hydrolysis is an especially important factor in the behavior of several metallic radionuclides in solution, and is observed in the transition, lanthanide, and actinide groups. For the actinide series, the +4 cations have the greatest charge/radius ratio and undergo hydrolysis most readily. Below pH 3, the

hydrolysis of Th^{4+} is negligible, but at higher pH, extensive hydrolysis occurs. Uranium(IV) undergoes hydrolysis in solution at a pH above 2.9 with $U(OH)_3^+$ being the predominant hydrolyzed species. Neptunium ions undergo hydrolysis in dilute acid conditions with evidence of polymer formation in acidic solutions less than 0.3 M. The hydrolysis of plutonium is the most severe, often leading to polymerization (see Section 14.10.4, "Polymerization"). In summary, the overall tendency of actinides to hydrolyze decreases in the order (Katz et al., 1986, p. 1145):

$$An^{+4} > AnO_2^{+2} > An^{+3} > AnO_2^{+1}$$

where "An" represents the general chemical symbol for an actinide.

For some cations, hydrolysis continues past the first reaction with water, increasing the number of hydroxide ions (OH^{-1}) associated with the cation in the aquo-hydroxo species:

$$U^{+4} + H_2O \rightarrow U(OH)^{+3} + H^{+1}$$

$$U(OH)^{+3} + H_2O \rightarrow U(OH)_2^{+2} + H^{+1}$$

This process can, in some cases, conclude with the precipitation of an insoluble hydroxide, such as ferric hydroxide. "Soluble hydrolysis products are especially important in systems where the cation concentrations are relatively low, and hence the range of pH relatively wide over which such species can be present and can profoundly affect the chemical behavior of the metal" (Baes and Mesmer, 1976, p. 3).

Solutions containing trace concentrations of metallic radionuclides qualify as an example of these systems. The form of hydrolysis products present can control important aspects of chemical behavior such as (Baes and Mesmer, 1976, p. 3):

- Adsorption of the radionuclide on surfaces, especially on mineral and soil particles.
- Tendency to coagulate colloidal particles.
- Solubility of the hydroxide or metal oxide.
- Extent of complex formation in solution.
- Extent of extraction from solution by various reagents.
- Ability to oxidize or reduce the radionuclide to another oxidation state.

Thus, a knowledge of the identity and stability of radionuclide ion hydrolysis products is important in understanding or predicting the chemical behavior of trace quantities of radionuclides in solution (Baes and Mesmer, 1976, p. 3). As the equilibrium equation indicates,

H^{+1} is produced as cations hydrolyze. Undesirable consequences of hydrolysis can, therefore, be minimized or eliminated by the addition of acid to the analytical mixture to reverse hydrolysis or prevent it from occurring. Numerous steps in radioanalytical procedures are performed at low pH to eliminate hydrolytic effects. It is also important to know the major and minor constituents of any sample, since hydrolysis effects are a function of pH and metal concentration. Thus, maintaining the pH of a high iron-content soil sample below pH 3.0 is important, even if iron is not the analyte.

14.10.4 Polymerization

The hydrolysis products of radionuclide cations described in the preceding section are monomeric—containing only one metal ion. Some of these monomers can spontaneously form polymeric metal hydroxo polymers in solution, represented by formation of the dimer (Birkett et al., 1988, p. 2.8-1):

$$2\ M(H_2O)_{x-1}(OH)^{+(n-1)} \rightarrow [(H_2O)_{x-2}M(OH)_2M(H_2O)_{x-2}]^{+2(n-1)} + 2\ H_2O$$

The polymers contain -OH-bridges between the metal ions that, under high temperature, prolonged aging, and/or high pH, can convert to -O-bridges, leading eventually to precipitation of hydrated metal oxides. Birkett et al. (1988) states that:

> "Formation of polymeric hydroxo species has been reported for most metals, although in some cases, the predominant species in solution is the monomer. Some metals form only dimers or trimers, while a few form much larger, higher-molecular-weight polymeric species.
>
> "Increasing the pH of a metal ion solution, by shifting the position of hydrolysis equilibrium ..., results in an increased concentration of hydrolyzed species ..., which in turn causes increased formation of polymeric species ... . Diluting a solution has two opposing effects on the formation of polymeric species:
>
> "(1) Because dilution of acidic solutions causes a decrease in H^{+1} concentration (i.e., an increase in pH), it causes a shift in the hydrolyzed equilibrium toward formation of hydrolyzed species.
>
> "(2) On the other hand, dilution decreases the ratio of polymeric to monomeric complexes in solution. For metals that form both monomeric and polymeric complexes, this means that monomeric species predominate beyond a certain level of dilution" (Birkett et al., 1988, p. 2.8-2).

Because this type of polymerization begins with hydrolysis of a cation, minimizing or eliminating polymerization can be achieved by the addition of acid to lower the pH of the analytical solution to prevent hydrolysis (Section 14.10.3, "Hydrolysis").

14.10.5 Complexation

Radionuclides exist as metal ions in solution, and many have a tendency to form stable complex ions with molecules or anions present as analytical reagents or impurities. The tendency to form complex ions is, to a considerable extent, an expression of the same properties that lead to hydrolysis; high positive charge on a +3 or +4 ion provides a strong driving force for the interaction with ligands (Katz et al., 1986, p. 1146) (Section 14.3, "Complexation").

Complex-ion formation by a radionuclide alters its form, introducing in solution additional species of the radionuclide whose concentrations depend on the magnitude of the formation constant(s). Alternate forms have different physical and chemical properties, and behave differently in separation techniques, such as extraction or partition chromatography. The behavior of alternate forms of radionuclides can present problems in the separation scheme that should be avoided if possible or addressed in the protocol. Some separation schemes, however, take advantage of the behavior of alternate radionuclide species formed by complexation, which can alter the solubility of the radionuclides in a solvent or their bonding to an ion-exchange resin (Section 14.3.4.2, "Separation by Solvent Extraction and Ion-Exchange Chromatography").

14.10.6 Radiocolloid Interference

The tendency of some radionuclides in solution, particularly tracer levels of radionuclides, to form radiocolloids, alters the physical and chemical behavior of those radionuclides (see Section 14.9.3.4, "Radiocolloid Formation"). Radioanalytical separations will not perform as expected in solutions containing radiocolloids, particularly as the solubility of the radionuclide species decreases.

Solutions containing large molecules, such as polymeric metal hydrolysis products, are more likely to form radiocolloids (Choppin et al., 1995, p. 243). "If the solution is kept at sufficiently low pH and extremely free of foreign particles, sorption and radiocolloid formation are usually avoided as major problems" (Choppin et al. 1995, p. 243). If tracer levels of radionuclides are present, trace impurities become especially significant in the radiochemical procedure, and should be minimized or avoided whenever possible (Crouthamel and Heinrich, 1971, p. 5493).

Crouthamel and Heinrich provide some specific insight into radiocolloidal interference in the equilibration problem:

> "The transition metals tend to form radiocolloids in solution, and in these heterogeneous systems the isotopic exchange reaction between a radiocolloid and inactive carrier added to the solution is sometimes slow and, more often, incomplete. Elements which show a strong tendency to form radiocolloids, even in macro concentrations and acid solutions, are titanium, zirconium, hafnium, niobium, tantalum, thorium, and protactinium, and, to a lesser degree, the rare earths. Other metals also may form radiocolloids, but generally offer a wider choice of valence states which may be stabilized in aqueous solutions" (Crouthamel and Heinrich, 1971, p. 5474).

14.10.7 Isotope Dilution Analysis

The basic concept of *isotope dilution analysis* is to measure the changes in specific activity of a substance upon its incorporation into a system containing an unknown amount of that substance. Friedlander et al. (1981), define *specific activity*:

> "Specific activity is defined as the ratio of the number of radioactive atoms to the total number of atoms of a given element in the sample (N^*/N). In many cases where only the ratios of specific activities are needed, quantities proportional to N^*/N, such as activity/mole, are referred to as specific activity" (Friedlander et al., 1981, p. 432).

For example, isotope dilution can be used to determine the amount of some inactive material A in a system (Wang et al., 1975). To the system containing x grams of an unknown weight of the inactive form of A, y grams of active material A^* of known activity D is added. The specific activity of the added active material, S_1, is given by:

$$S_1 = D/y$$

After ensuring isotopic exchange, the mixture of A and A^* is isolated, but not necessarily quantitatively, and purified. The specific activity, S_2, is measured. Owing to the conservation of matter,

$$S_2 = D/(x + y)$$

and by substituting for S_1y for D and rearranging, the amount x of inactive A is given as

$$x = y(S_1/S_2 - 1)$$

However, this equation is valid only if complete isotopic exchange has occurred, a task not always easy to achieve.

14.10.8 Masking and Demasking

Masking is the prevention of reactions that are normally expected to occur through the presence or addition of a masking reagent. Masking reactions can be represented by the general reversible equation:

$$A + Ms - A \cdot Ms$$

where A is the normal reacting molecule or ion, and Ms is the masking agent. The decreased concentration of A at equilibrium determines the efficiency of masking. An excess of masking agent favors the completeness of masking, as expected from LeChatelier's Principle. Feigl (1936, p. 409) has described *masking reagent* and the *masking* of a reaction as follows: "... the concentration of a given ion in a solution can be so diminished by the addition of substances which unite with the ion to form complex salts that an ion product sufficient to form a precipitate or cause a color reaction is no longer obtained. Thus we speak of the *masking* of a reaction and call the reagent responsible for the disappearance of the ions necessary for the reaction, the *masking reagent*." The concepts of masking and demasking are discussed further in Perrin (1979. pp. 600-643) and in Dean (1995, pp. 2.9-2.15).

Masking techniques are frequently used in analytical chemistry because they often provide convenient and efficient methods to avoid the effects of unwanted components of a system without having to separate the interferant physically. Therefore, the selectivity of many analytical techniques can be increased through masking techniques. For example, copper can be prohibited from carrying on ferric hydroxide at pH 7 by the addition of ammonium ions to complex the copper ions. Fe^{3+} and Al^{3+} both interfere with the extraction of the +3 actinides and lanthanides in some systems, but Fe^{3+} can be easily masked through reduction with ascorbic acid, and Al^{3+} can be masked through complexation with fluoride ion (Horwitz et al., 1993 and 1994). In another example, uranium can be isolated on a U/TEVA column (Eichrom Industries, Inc., Darien, IL) from nitric acid solutions by masking the tetravalent actinides with oxalic acid; the tetravalent actinides are complexed and pass through the column, whereas uranium is extracted (SpecNews, 1993). Strontium and barium can be isolated from other metals by cation exchange from a solution of water, pyridine, acetic acid and glycolic acid. The other metals form neutral or negative complexes and pass through the cation column, while strontium and barium are retained

(Orlandini, 1972). Masking phenomena are present in natural systems as well. It has been demonstrated that humic and fulvic acids can complex heavy metals such that they are no longer bioavailable and are, therefore, not taken up by plants. Tables 14.17 and 14.18 list common masking agents.

TABLE 14.17 — Masking agents for ions of various metals [1]

Metal	Masking Agent
Ag	Br^-, citrate, Cl^-, CN^-, I^-, NH_3, SCN^- $S_2O_3^{-2}$, thiourea, thioglycolic acid, diethyldithiocarbamate, thiosemicarbazide, bis(2-hydroxyethyl)dithiocarbamate
Al	Acetate, acetylacetone, BF_4^-, citrate, $C_2O_4^{-2}$, EDTA, F^-, formate, 8-hydroxyquinoline-5-sulfonic acid, mannitol, 2,3-mercaptopropanol, OH^-, salicylate, sulfosalicylate, tartrate, triethanolamine, tiron
As	Citrate, 2,3-dimercaptopropanol, $NH_2OH{\cdot}HCl$, OH^-, S_2^{-2}, tartrate
Au	Br^-, CN^-, NH_3, SCN^-, $S_2O_3^{-2}$, thiourea
Ba	Citrate, cyclohexanediaminetetraacetic acid, *N,N*-dihydroxyethylglycine, EDTA, F^-, SO_4^{-2}, tartrate
Be	Acetylacetone, citrate, EDTA, F^-, sulfosalicylate, tartrate
Bi	Citrate, Cl^-, 2,3-dimercaptopropanol, dithizone, EDTA, I^-, OH^-, $Na_5P_3O_{10}$, SCN^-, tartrate, thiosulfate, thiourea, triethanolamine
Ca	BF_4^-, citrate, *N,N*-dihydroxyethylglycine, EDTA, F^-, polyphosphates, tartrate
Cd	Citrate, CN^-, 2,3-dimercaptopropanol, dimercaptosuccinic acid, dithizone, EDTA, glycine, I^-, malonate, NH_3, 1,10-phenanthroline, SCN^-, $S_2O_3^{-2}$, tartrate
Ce	Citrate, *N,N*-dihydroxyethylglycine, EDTA, F^-, PO_4^{-3}, reducing agents (ascorbic acid), tartrate, tiron
Co	Citrate, CN^-, diethyldithiocarbamate, 2,3-dimercaptopropanol, dimethylglyoxime, ethylenediamine, EDTA, F^-, glycine, H_2O_2, NH_3, NO_2^-, 1,10-phenanthroline, $Na_5P_3O_{10}$, SCN^-, $S_2O_3^{-2}$, tartrate
Cr	Acetate, (reduction with) ascorbic acid + KI, citrate, *N,N*-dihydroxyethylglycine, EDTA, F^-, formate, NaOH + H_2O_2, oxidation to CrO_4^{-2}, $Na_5P_3O_{10}$, sulfosalicylate, tartrate, triethylamine, tiron
Cu	Ascorbic acid + KI, citrate, CN^-, diethyldithiocarbamate, 2,3-dimercaptopropanol, ethylenediamine, EDTA, glycine, hexacyanocobalt(III)(3-), hydrazine, I^-, NaH_2PO_2, $NH_2OH{\cdot}HCl$, NH_3, NO_2^-, 1,10-phenanthroline, S^{-2}, SCN^- + SO_3^{-2}, sulfosalicylate, tartrate, thioglycolic acid, thiosemicarbazide, thiocarbohydrazide, thiourea
Fe	Acetylacetone, (reduction with) ascorbic acid, $C_2O_4^{-2}$, citrate, CN^- 2,3-dimercaptopropanol, EDTA, F^-, NH_3, $NH_2OH{\cdot}HCl$, OH^-, oxine 1,10-phenanthroline, 2,2'-bipyridyl, PO_4^{-3}, $P_2O_7^{-4}$, S^{-2}, SCN^-, $SnCl_2$, $S_2O_3^{-2}$, sulfamic acid, sulfosalicylate, tartrate, thioglycolic acid, thiourea, tiron, triethanolamine, trithiocarbonate
Ga	Citrate, Cl^-, EDTA, OH^-, oxalate, sulfosalicylate, tartrate
Ge	F^-, oxalate, tartrate
Hf	See Zr
Hg	Acetone, (reduction with) ascorbic acid, citrate, Cl^-, CN^-, 2,3-dimercaptopropan-1-ol, EDTA, formate, I^-, SCN^-, SO_3^{-2}, tartrate, thiosemicarbazide, thiourea, triethanolamine
In	Cl^-, EDTA, F^-, SCN^-, tartrate thiourea, triethanolamine
Ir	Citrate, CN^-, SCN^-, tartrate, thiourea
La	Citrate, EDTA, F^-, oxalate, tartrate, tiron

	Metal	Masking Agent
3266	Mg	Citrate, $C_2O_4^{-2}$, cyclohexane-1,2-diaminetetraacetic acid, *N,N*-dihydroxyethylglycine, EDTA, F^-, glycol, hexametaphosphate, OH^-, $P_2O_7^{-4}$, triethanolamine
3267	Mn	Citrate, CN^-, $C_2O_4^{-2}$, 2,3-dimercaptopropanol, EDTA, F^-, $Na_5P_3O_{10}$, oxidation to MnO_4^-, $P_2O_7^{-4}$, reduction to Mn(II) with $NH_2OH{\cdot}HCl$ or hydrazine, sulfosalicylate, tartrate, triethanolamine, triphosphate, tiron
3268	Mo	Acetylacetone, ascorbic acid, citrate, $C_2O_4^{-2}$, EDTA, F^-, H_2O_2, hydrazine, mannitol, $Na_5P_3O_{10}$, $NH_2OH{\cdot}HCl$, oxidation to molybdate, SCN^-, tartrate, tiron, triphosphate
3269	Nb	Citrate, $C_2O_4^{-2}$, F^-, H_2O_2, OH^-, tartrate
3270	Nd	EDTA
3271	NH_4^+	HCHO
3272	Ni	Citrate, CN^-, *N,N*-dihydroxyethylglycine, dimethylglyoxime, EDTA, F^-, glycine, malonate, $Na_5P_3O_{10}$, NH_3 1,10-phenanthroline, SCN^-, sulfosalicylate, thioglycolic acid, triethanolamine, tartrate
3273	Np	F^-
3274	Os	CN^-, SCN^-, thiourea
3275	Pa	H_2O_2
3276	Pb	Acetate, $(C_6H_5)_4AsCl$, citrate, 2,3-dimercaptopropanol, EDTA, I^-, $Na_5P_3O_{10}$, SO_4^{-2}, $S_2O_3^{-2}$, tartrate, tiron, tetraphenylarsonium chloride, triethanolamine, thioglycolic acid
3277	Pd	Acetylacetone, citrate, CN^-, EDTA, I^-, NH_3, NO_2^-, SCN^-, $S_2O_3^{-2}$, tartrate, triethanol-amine
3278	Pt	Citrate, CN^-, EDTA, I^-, NH_3, NO_2^-, SCN^-, $S_2O_3^{-2}$, tartrate, urea
3279	Pu	Reduction to Pu(IV) with sulfamic acid
3280	Rare Earths	$C_2O_4^{-2}$, citrate, EDTA, F^-, tartrate
3281	Re	Oxidation to perrhenate
3282	Rh	Citrate, tartrate, thiourea
3283	Ru	CN^-, thiourea
3284	Sb	Citrate, 2,3-dimercaptopropanol, EDTA, I^-, OH^-, oxalate, S^{-2}, S_2^{-2}, $S_2O_3^{-2}$, tartrate, triethanolamine
3285	Sc	Cyclohexane-1,2-diaminetetraacetic acid, F^-, tartrate
3286	Se	Citrate, F^-, I^-, reducing agents, S^{-2}, SO_3^{-2}, tartrate
3287	Sn	Citrate, $C_2O_3^{-2}$, 2,3-dimercaptopropanol, EDTA, F^-, I^-, OH^-, oxidation with bromine water, PO_4^{-3}, tartrate, triethanolamine, thioglycolic acid
3288	Ta	Citrate, F^-, H_2O_2, OH^-, oxalate, tartrate
3289	Te	Citrate, F^-, I^-, reducing agents, S^{-2}, sulfite, tartrate
3290	Th	Acetate, acetylacetone, citrate, EDTA, F^-, SO_4^{-2}, 4-sulfobenzenearsonic acid, sulfosalicylic acid, tartrate, triethanolamine
3291	Ti	Ascorbic acid, citrate, F^-, gluconate, H_2O_2, mannitol, $Na_5P_3O_{10}$, OH^-, SO_4^{-2}, sulfosalicylic, acid, tartrate, triethanolamine, tiron
3292	Tl	Citrate, Cl^-, CN^-, EDTA, HCHO, hydrazine, $NH_2OH{\cdot}HCl$, oxalate, tartrate, triethanolamine
3293	U	Citrate, $(NH_4)_2CO_3$, $C_2O_4^{-2}$, EDTA, F^-, H_2O_2, hydrazine + triethanolamine, PO_4^{-3}, tartrate
3294	V	(reduction with) Ascorbic acid, hydrazine, or $NH_2OH{\cdot}HCl$, CN^-, EDTA, H_2O_2, mannitol, oxidation to vanadate, triethanolamine, tiron

Metal	Masking Agent
W	Citrate, F^-, H_2O_2, hydrazine, $Na_5P_3O_{10}$, $NH_2OH{\cdot}HCl$, oxalate, SCN^-, tartrate, tiron, triphosphate, oxidation to tungstate
Y	Cyclohexane-1,2-diaminetetraacetic acid, F^-
Zn	Citrate, CN^-, *N,N*-dihydroxyethylglycine, 2,3-dimercaptopropanol, dithizone, EDTA, F^-, glycerol, glycol, hexacyanoferrate(II)(4-), $Na_5P_3O_{10}$, NH_3, OH^-, SCN^-, tartrate, triethanolamine
Zr	Arsenazo, carbonate, citrate, C_2O^{-2}, cyclohexane-1,2-diaminetetraacetic acid, EDTA, F^-, H_2O_2, PO_4^{-3}, $P_2O_7^{-4}$, pyrogallol, quinalizarinesulfonic acid, salicylate, $SO_4^{-2} + H_2O_2$, sulfosalicylate, tartrate, triethanolamine

(1) Compiled from Perrin (1979, pp. 609-611) and Dean (1995, pp. ?)

TABLE 14.18 — Masking agents for anions and neutral molecules

Anion or Neutral Molecule	Masking Agent
Boric Acid	F^-, glycol, mannitol, tartrate, and other hydroxy acids
Br^-	Hg(II)
Br_2	Phenol, sulfosalicylic acid
BrO_3^-	Reduction with arsenate(III), hydrazine, sulfite, or thiosulfate
Chromate(VI)	Reduction with arsenate(III), ascorbic acid, hydrazine, hydroxylamine, sulfite, or thiosulfate
Citrate	Ca(II)
Cl^-	Hg(II), Sb(III)
Cl_2	Sulfite
ClO_3^-	Thiosulfate
ClO_4^-	Hydrazine, sulfite
CN^-	HCHO, Hg(II), transition-metal ions
EDTA	Cu(II)
F^-	Al (III), Be(II), boric acid, Fe(III), Th(IV), Ti(IV), Zr(IV)
$Fe(CN)_3^{-3}$	Arsenate(III), ascorbic acid, hydrazine, hydroxylamine, thiosulfate
Germanic Acid	Glucose, glycerol, mannitol
I^-	Hg(II)
I_2	Thiosulfate
IO_3^-	Hydrazine, sulfite, thiosulfate
IO_4^-	Arsenate(III), hydrazine, molybdate(VI), sulfite, thiosulfate
MnO_4^-	Reduction with arsenate(III), ascorbic acid, azide, hydrazine, hydroxylamine, oxalic acid,
MoO_4^{-2}	sulfite, or thiosulfate
NO_2^-	Citrate, F^-, H_2O_2, oxalate, thiocyanate + Sn(II)
Oxalate	Co(II), sulfamic acid, sulfanilic acid, urea
Phosphate	Molybdate(VI), permanganate
S	Fe(III), tartrate
S^{-2}	CN^-, S^{2-}, sulfite
Sulfate	Permanganate + sulfuric acid, sulfur
Sulfite	Cr(III) + heat
SO_6^{-2}	HCHO, Hg(II), permanganate + sulfuric acid
Se and its anions	Ascorbic acid, hydroxylamine, thiosulfate

Anion or Neutral Molecule	Masking Agent
TeI^-	Diaminobenzidine, sulfide, sulfite
Tungstate	Citrate, tartrate
Vanadate	Tartrate

(1) Compiled from Perrin (1979, p. 612) and Dean (1995)

Demasking refers to any procedure that eliminates the effect of a masking agent already present in solution. There are a variety of methods for demasking, including changing the pH of the solution and physically removing, destroying, or displacing the masking agent. The stability of most metal complexes depends on pH, so simply raising or lowering the pH is frequently sufficient for demasking. Another approach to demasking involves the formation of new complexes or compounds that are more stable than the masked species. For example, boric acid commonly is used to demask the fluoride complexes of Sn^{4+} or Mo^{6+}, and hydroxide is used to demask the thiocyanate complexes of Fe^{3+}. In addition, it might be possible to destroy the masking agent in solution through a chemical reaction (i.e., via the oxidation of EDTA in acidic solutions by permanganate or another strong oxidizing agent).

14.10.9 Review of Specific Radionuclides

14.10.9.1 Americium

Americium is a metal of the actinide series which is produced synthetically by neutron activation of uranium or plutonium followed by beta decay.

Isotopes

Twenty isotopes of americium are known, ^{232}Am through ^{248}Am, including three metastable states. All isotopes are radioactive. ^{243}Am and ^{241}Am, alpha emitters, are the longest lived with a half-lives of 7,380 years and 432.7 years, respectively. ^{241}Am and ^{243}Am also undergo spontaneous fission. ^{242m}Am has a half-life of 141 years, and the half-lives of the remaining isotopes are measured in hours, minutes, or seconds. ^{241}Am is the most common isotope of environmental concern.

Occurrence

None of the isotopes of americium occur naturally. It is produced synthetically by neutron bombardment of ^{238}U or ^{239}Pu followed by beta decay of the unstable intermediates. ^{241}Am is

found in military wastes and can be extracted from reactor wastes. Some industrial ionization sources also contain americium. Decay of ^{241}Pu injected in the atmosphere during weapons testing contributes to the presence of ^{241}Am.

The silver metal is prepared by reduction of americium fluoride (AmF_3) or americium oxide (AmO_2) with active metals at high temperatures and is purified by fractional distillation, taking advantage of its exceptionally high vapor pressure compared to other transuranium elements. Kilogram quantities of ^{241}Am are available, but only 10 to 100 g quantities of ^{243}Am are prepared.

Soft gamma emission from ^{241}Am is used to measure the thickness of metal sheets and metal coatings, the degree of soil compaction, sediment concentration in streams, and to induce X-ray fluorescence in chemical analysis. As an alpha emitter, it is mixed with beryllium to produce a neutron source for oil-well logging and to measure water content in soils and industrial process streams. The alpha source is also used to eliminate static electricity and as an ionization source in smoke detectors.

Solubility of Compounds

Among the soluble salts are the nitrate, halides, sulfate, and chlorate of americium(III). The fluoride, hydroxide, and oxalate are insoluble. The phosphate and iodate are moderately soluble in acid solution. Americium(VI) is precipitated with sodium acetate to produce the hydrate, $NaAmO_2(C_2H_3O_2)_3 \cdot xH_2O$.

Review of Properties

The study of the properties of americium is very difficult because of the intense alpha radiation emitted by ^{241}Am and ^{243}Am, but some properties are known. Americium metal is very ductile and malleable but highly reactive and unstable in air, forming the oxide. It is considered to be a slightly more active metal than plutonium and is highly reactive combing directly with oxygen, hydrogen, and halides to form the respective compounds, AmO_2, AmH_3, and AX_3. Alloys of americium with platinum, palladium, and iridium have been prepared by hydrogen reduction of americium oxide in the presence of the finely divided metals.

Unless the transuranium elements are associated with high-level gamma emission, the principal toxicological problems associated with the radionuclides are the result of internal exposure after inhalation or ingestion. When inhaled or ingested, they are about equally distributed between bone tissue and the liver. At high doses transuranics lead to malignant tumors years later. In addition, large quantities of ^{241}Am could conceivably lead to criticality problems, producing

external radiation hazards or neutron exposure from (α,n) reactions. ^{241}Am is also a gamma emitter.

Americium is generally thought to be absorbed by all common rocks at pH values found in the environment. Complexation of Am(III) by naturally occurring ligands, however, would be expected to strongly reduce its adsorption.

Solution Chemistry

Americium can exist in solution in the +3, +4, +5, and +6 oxidation states. Simple aqueous ions of Am^{+3} and AmO_2^{+2} (VI oxidation state) are stable in dilute acid, but Am^{+3} is the predominant oxidation state. Free radicals produced by radiolysis of water by alpha particles reduce the higher states spontaneously to Am^{+3}. The +3 oxidation state exists as $Am(OH)_3$ in alkaline solution. Simple tetravalent americium is unstable in mineral acid solutions, disproportionating rapidly to produce Am^{+3} and AmO_2^{+1} [Am(V)] in nitric and perchloric acid solutions. Conversely, dissociation of $Am(OH)_4$ or AmO_2 [both Am(IV)] in sulfuric acid solutions produces solutions containing Am^{+3} and AmO_2^{+2}. Stability is provided by complexation with fluoride ions and oxygen-containing ligands such as carbonate and phosphate ions. The AmO_2^{+1} ion also disproportionates in acid solutions to yield Am^{+3} and AmO_2^{+2}, but the process for ^{241}Am is so slow that radiation-induced reduction dominates. Evidence exists for the presence of Am^{+7} in alkaline solutions from the oxidation of AmO_2^{+2}.

OXIDATION-REDUCTION BEHAVIOR. Although disproportionation reactions convert the +4 and +5 oxidation states into the +3 and +6 states, radiolysis eventually converts the higher oxidation state into Am^{+3}. Redox processes are used, however, to produce solutions of alternate oxidation states and to equilibrate the forms of americium into a common state, usually +3, but sometimes +6.

The +4 state is reduced to Am^{+3} by iodide. In dilute, non-reducing solutions, peroxydisulfate ($S_2O_8^{-2}$) oxidizes both the +3 and +5 states to the +6 state. Ce^{+4} and ozone (O_3) oxidizes the +5 state to +6 in perchloric acid solution. Electrolytic oxidation of Am^{+3} to AmO_2^{+2} occurs in phosphoric, nitric, and perchloric acid solutions and solutions of sodium bicarbonate (Na_2CO_3). The latter ion is reduced to Am^{+3} by iodide, hydrogen peroxide, and the nitrite ion (NO_2^{-1}).

COMPLEXATION. The +3 oxidation state forms complexes in the following order of strength (in aqueous solution): $F^- > H_2PO_4^- > SCN^- > NO_3^- > Cl^-$. Both americium (+3) and (IV) form complexes with organic chelants. These are stable in aqueous and organic solvents. Americium

(IV) however can be easily reduced unless special oxidizing conditions are maintained." The AmO_2^{+2} ion also forms significant complex ions with nitrate, sulfate, and fluoride ions.

HYDROLYSIS. The actinide elements are known for their tendency to hydrolyze and, in many cases, form insoluble polymers. In the predominant +3 oxidation state in solution, americium, with its large radius, has the least tendency of the +3 actinides to hydrolyze; yet, hydrolysis is expected to occur with some polymerization. Hydrolysis that does occur is complicated and depends on the nature of the cations present and may start at pH values as low as 0.5-1.0. In contrast, the AmO_2^{+2}, like all actinyl ions, undergoes hydrolysis to an appreciable extent. The tendency to form polymers of colloidal dimensions, however, appears to be small relative to other actinide ions in the +6 oxidation state. Precipitation occurs early on after relatively small polymeric aggregates form in solution. The strong tendency to form insoluble precipitates after a small amount of hydrolysis makes characterization of the water-soluble polymers a difficult problem.

RADIOCOLLOIDS. At trace concentrations, a colloidal form of Am^{+2} can easily be prepared, so steps should be taken to avoid its formation during analytical procedures. At high pH ranges, colloids form from the $Am(OH)_3$, and at lower pH ranges through adsorption of Am^{+3} onto foreign particles. Their formation depends on storage time, pH, and ionic strength of the solution.

Dissolution of Samples

Americium is generally dissolved from irradiated reactor fuels, research compounds, and soil, vegetation, and biological samples. Spent fuel elements may be difficult to dissolve but eventually yield to digestion with hydrofluoric acid, nitric acid, or sulfuric acid. Aqua regia is used if platinum is present, and hydrochloric acid with an oxidizing agent such as sodium chlorate. Perchloric acid, while a good solvent for uranium, reacts too vigorously. Sodium hydroxide-peroxide is a good basic solvent. Research compounds, usually salts, yield to hot concentrated nitric or sulfuric acid. Soil samples are digested with concentrated nitric acid, hydrofluoric acid, or hydrochloric acid. Vegetation and biological samples are commonly wet ashed, and the residue is treated with nitric acid.

Separation Methods

The separation of americium, particularly from other transuranics, is facilitated by the exceptional stability of Am(III) compared to the trivalent ions of other actinides, which more readily convert to higher oxidation states under conditions that americium remains trivalent.

PRECIPITATION AND COPRECIPITATION. Coprecipitation with lanthanum fluoride (LaF_3) is achieved after reduction of higher oxidation states to Am(III). Select oxidation of other transuranic elements such as neptunium and plutonium to the IV or VI oxidation states solubilizes these radionuclides leaving americium in the insoluble form. Although coprecipitation with rare earths as fluorides or hydroxides from a bicarbonate solution of americium(VI), is used to purify americium, it is not as effective as ion-exchange procedures. Other coprecipitating agents for americium(III) include thorium oxalate [$Th(C_2O_4)_2$], calcium oxalate (CaC_2O_4), ferric hydroxide [$Fe(OH)_3$), and lanthanum potassium sulfate [$LaK(SO_4)_2$]. Americium(IV) is also coprecipitated with these reagents as well as with zirconium phosphate [$Zr_3(PO_4)_2$]. Americium(VI) is not coprecipitated with any of these reagents but with sodium uranyl acetate [$NaUO_2(C_2H_3O_2)_2$].

SOLVENT EXTRACTION. Organic solvents and chelating agents are available for separating americium from other radionuclides by selectively extracting either americium or the alternate radionuclide from aqueous solutions into an organic phase. Tributyl phosphate (TBP) in kerosene or thenoyltrifluoroacetone (TTA) in xylene removes most oxidation states of neptunium and plutonium from americium(III) in the presence of dilute nitric acid. The addition of sodium nitrate (6 M) tends to reverse the trend making americium more soluble in TBP than uranium, neptunium, or plutonium radionuclides. Di(2-ethylhexyl)phosphoric acid (HDEHP) in toluene is highly effective in extracting americium(III) and is used in sample preparation for alpha spectroscopic analysis.

Recently, solvent extraction chromatography has offered an efficient, easy technique for rapidly separating americium and other transuranic elements. A process using octylphenyl-N,N-diisobutyl carbamoylphoshpine oxide (CMPO) in dissolved TBP and fixed on an inert polymeric resin matrix has been used to isolate americium(III). The column is loaded with 2 M nitric acid, and americium is eluted with 4 M hydrochloric acid. It is important to note that iron, found in most environmental samples, does not effect the americium isolation if the iron is kept in the +2 oxidation state. The ferric ion (Fe^{+3}) is detrimental to the separation.

ION EXCHANGE. Separation of americium can be achieved by cation-exchange chromatography. Any of its oxidation states absorb on a cation resin in dilute acid solution, but the higher oxidation states are not important in cation-exchange separations because they are unstable toward reduction to the +3 state. Generally, americium(III) is the last tripositive ion among the actinides eluted from a cation-exchange matrix, although the order may not be maintained under all conditions. Many eluting agents are available for specific separations. Concentrated hydrochloric acid, for example, has been used for separating actinides such as americium from the lanthanides. Anion-exchange chromatography has been widely used for separating

3489 americium. Anionic complexes of americium(III) form at high chloride concentrations, providing
3490 a chemical form that is easily exchanged on an anion-exchange column. The column can be
3491 eluted using dilute hydrochloric acid or a dilute hydrochloric acid/ammonium thiocyanate
3492 solution. Anion-exchange separations of americium are also realized with columns prepared with
3493 concentrated nitric acid solutions. The sequential separation of the actinides is accomplished
3494 readily using anion-exchange chromatography. Americium, plutonium, neptunium, thorium,
3495 protactinium, curium, and uranium can all be separated by the proper application of select acid or
3496 salt solutions to the column.

3497 ELECTRODEPOSITION. Americium can be electrodeposited for alpha spectrometry measurement
3498 on a highly-polished platinum cathode. The sample is dissolved in a dilute hydrochloric acid
3499 solution that has been adjusted to a pH of about six with ammonium hydroxide solution using
3500 methyl red indicator. The process runs for one hour at 1.2 amps.

3501 Methods of Analysis

3502 ^{241}Am is detected and quantified by either alpha counting or gamma spectroscopy. Trace
3503 quantities of ^{241}Am are analyzed by alpha counting, after separation from interfering
3504 radionuclides by solvent extraction, coprecipitation, or ion-exchange chromatography. The
3505 isolated radionuclide is collected by coprecipitation, filtered, and mounted on a planchet or
3506 electroplated onto a platinum electrode for counting by alpha spectrometry. ^{243}Am is added to the
3507 analytical solution as a tracer to measure chemical recovery. ^{241}Am in bulk soil samples can be
3508 determined by gamma spectroscopy.

3509 Compiled from: Ahrland, 1986; Baes and Mesmer, 1976; Choppin et al., 1995; Considine
3510 and Considine, 1983; Cotton and Wilkinson, 1988; DOE, 1990 and 1997, 1995; 1997;
3511 Ehmann and Vance, 1991; Greenwood and Earnshaw, 1984; Haissinsky and Adolff, 1965;
3512 Katz et al., 1986; Lindsay, 1988; Metz and Waterbury, 1962; NEA, 1982; SCA, 2001;
3513 Penneman, 1994; Penneman and Keenan, 1960; Schulz and Penneman, 1986; Seaborg and
3514 Loveland, 1990; Horwitzetal, 1993.

3515 ### 14.10.9.2 Cesium

3516 Cesium is the last member of the naturally occurring alkali metals in group IA of the periodic
3517 table with an atomic number of 55. As such, its radiochemistry is simplified because the Group
3518 IA metals form only +1 ions. Elemental cesium is a very soft, silver-white metallic solid in the
3519 pure state with a melting point of only 28.5 °C. It tarnishes quickly to a golden-yellow color

when exposed to small amounts of air. In larger amounts of air it ignites spontaneously. It is normally stored under xylente/toluene to prevent contact with air.

Isotopes

Cesium isotopes of mass number 112 to 148 have been identified. ^{133}Cs is the only stable isotope. ^{134}Cs and ^{137}Cs are the only two isotopes of significance from an environmental perspective. Both are formed from the nuclear fission process. Their half-lives are 2.06 and 30.17 years, respectively.

Occurrence

Cesium is widely distributed in the Earth's crust with other alkali metals. In granite and sedimentary rocks the concentration is less than 7 ppm. In seawater it is about 0.002 ppm, but in mineral springs the concentration may be greater than 9 mg/L. Cesium is found in complex minerals such as carnallite, a potassium and magnesium chloride mineral that contains small percentages of cesium compounds; lepidolite ores, a lithium aluminum silicate; and pollucite, a cesium-rich ore of the oxides of cesium, aluminum, and silicon. ^{137}Cs is produced in nuclear fission and occurs in atmospheric debris from weapons tests and accidents. It is a very important component of radioactive fallout; and because of its moderately long half-life and high solubility, it is a major source of long-lived external gamma radiation from fallout. It accounts for 30 percent of the gamma activity of fission products stored for one year, 70 percent in two years, and 100 percent after five years.

Cesium metal is not produced on a commercial scale. It is isolated from its minerals, however, by acid extraction, fusion with alkaline fluxes, or direct reduction of an ore to metallic cesium. Extraction and fusion yield a cesium salt, which is treated by oxidation-reduction processes to make the pure metal. The salt is either roasted with carbon, heated with calcium or lithium, or electrolyzed as a melt to reduce the cation to pure cesium. Special equipment should be used in these processes because of the very reactive chemical nature of the metal.

Metallic cesium is used in photoelectric cells, spectrographic instruments, scintillation counters, and other optical and detecting devices, sometimes alloyed with calcium, strontium, or barium to facilitate handling. Its most recognized use is in the atomic clock that serves to define the second. Cesium has been considered as a fuel in ion-propulsion engines for deep space travel and as a heat-transfer medium for some applications. ^{137}Cs has replaced ^{60}Co in the treatment of cancer and has been used in industrial radiography for the control of welds. Cesium compounds are used in glass and ceramic production, as an absorbent in carbon dioxide production plants, and in the

preparation of density gradients for the separation of macromolecules by centrifugation. ^{37}Cs is also used commercially as a sealed source in liquid scintillation spectrometers. The 661 keV gamma ray it emits is used to create an electron (Compton effect) distribution which allows the degree of sample quench to be determined.

Solubility of Compounds

Most cesium salts are very soluble in water and dilute acids. Among the salts of common anions, the notable exceptions are cesium perchlorate and periodate ($CsClO_4$ and $CsIO_4$). Several cesium compounds of large anions are insoluble. Examples include the following: silicotungstate [$Cs_8SiW_{12}O_{42}$], permanganate ($CsMnO_4$), chloroplatinate (Cs_2PtCl_6), tetraphenylborate [$CsB(C_6H_5)_4$], alum [$CsAl(SO_4)_2$], and cobaltnitrate complex [$Cs_3Co(NO_3)_6$].

Review of Properties

Cesium is the most active and electropositive of all the metals. It forms compounds with most inorganic and organic anions; it readily forms alums with all the trivalent cations that are found in alums. The metal readily ionizes, and in ammonia solutions and it is a powerful reducing agent. When exposed to moist air, it tarnishes initially forming oxides and a nitride and then quickly melts or bursts into flame. With water the reaction is violent. Cesium reacts vigorously with halogens and oxygen, and it is exceptional among the alkali metals in that it can form stable polyhalides such as CsI_3. Reaction with oxygen forms a mixture of oxides: cesium oxide (Cs_2O), cesium peroxide (Cs_2O_2), and cesium superoxide (CsO_2). The toxicity of cesium compounds is generally not important unless combined with another toxic ion.

^{137}Cs, introduced into the water environment as cations, is attached to soil particles and can be removed by erosion and runoff. However, soil sediment particles act as sinks for ^{137}Cs, and the radionuclide is almost irreversible bound to mica and clay minerals in freshwater environments. It is unlikely that ^{137}Cs will be removed from these sediments under typical environmental conditions. Solutions of high ionic strength as occur in estuarine environments might provide sufficient exchange character to cause cesium to become mobile in the ecosphere.

Solution Chemistry

The cesium ion exists in only the +1 oxidation state, and its solution chemistry is not complicated by oxidation-reduction reactions. As a result, it undergoes complete, rapid exchange with carriers in solution. The cesium ion is colorless in solution and is probably hydrated as a hexaaquo complex.

COMPLEXATION. Cesium ions form very few complex ions in solution. The few that form are primarily with nitrogen-donor ligands or beta-diketones. Anhydrous beta-diketones are insoluble in water, but in the presence of additional coordinating agents, including water, they become soluble in hydrocarbons. One solvent-extraction procedure from aqueous solutions is based on chelation of cesium with 1,1,1-trifluoro-3-(2′-thenoyl)acetone (TTA) in a hydrocarbon solvents. Cesium is sandwiched between crown ligands, associated with the oxygen atoms of the ether, in $[Cs_9(18\text{-}C\text{-}6)_{14}]^{+9}$.

HYDROLYSIS. With the small charge and large radius of the cesium ion, hydrolysis reactions are inconsequential.

ADSORPTION. When cesium is present in extremely low concentrations, even in the presence of 2 M acid, adsorption on the walls of glass and plastic containers leads to complications for the radioanalyst. Half the activity of cesium radionuclides, for example, can be lost from acid solutions stored for one month in these containers. Experiments indicate that addition of 1 µg cesium carrier per mL of solution is sufficient to stabilize acid solutions for six months.

Dissolution of Samples

Radiochemists generally dissolve cesium samples from irradiated nuclear fuel, activated cesium salts, natural water, organic material, agriculture material, and soils. Nuclear fuel samples are generally dissolved in HCl, HNO_3, HF, or a combination of these acids. Care should be taken to ensure that the sample is representative if ^{137}Cs has been used as a burn-up monitor. Precautions should also be taken with these samples to prevent loss of cesium because of leaching or incomplete sample dissolution. Most cesium salts dissolve readily in water and acid solutions. In water samples, the cesium might require concentration, preferably by ion exchange, or by precipitation or coprecipitation if interfering ions are present. Organic materials are either decomposed by HNO_3 or dry ashed, and the cesium is extracted with hot water or hot acid solution. Extraction and leaching procedure have been use to assess exchangeable or leachable cesium using ammonium acetate solutions or acid solutions, but soils are generally completely solubilized in HNO_3, HCl, HF, H_2SO_4, or a mixture of these acids in order to account for all the cesium in a soil sample.

Separation Methods

PRECIPITATION AND COPRECIPITATION. Cesium is separated and purified by several precipitation and coprecipitation methods using salts of large anions. Gravimetric procedures rely on precipitation to collect cesium for weighing, and several radiochemical techniques isolate cesium

radionuclides for counting by precipitation or coprecipitation. Cesium can be precipitated, or coprecipitated in the presence of cesium carrier, by the chlorate, cobaltinitrate, platinate, and tetraphenylborate ions. Other alkali metals interfere and should be removed before a pure insoluble compound can be collected. Cesium can be isolated from other alkali metals by precipitation as the silicotungstate. The precipitate can be dissolved in 6 M sodium hydroxide, and cesium can be further processed by other separation procedures. The tetraphenylborate procedure first removes other interfering ions by a carbonate and hydroxide precipitation in the presence of iron, barium, lanthanum, and zirconium carriers. Cesium is subsequently precipitated by the addition of sodium tetraphenylborate to the acidified supernatant. Alum also precipitates cesium from water samples in the presence of macro quantities of the alkali metals. Trace quantities of cesium radionuclides are precipitated using stable cesium as a carrier.

ION EXCHANGE. The cesium cation is not retained by anion-exchange resins and does not form a suitable anion for anion-exchange chromatography. The process is used, however, to separate cesium from interfering ions that form anionic complexes. Cesium elutes first in these procedures. Cesium is retained by cation-exchange resins. Because the cesium ion has the largest ionic radius and has a +1 charge, it is less hydrated than most other cations. Therefore, cesium has a small hydrated radius and can approach the cation exchange site to form a strong electrostatic association with the ion-exchange resin. Binding of alkali metal ion to cation exchange resins follows the order: $Cs^{+1}>Rb^{+1}>K^{+1}>Na^{+1}>Li^{+1}$. Cesium is generally the last alkali metal ion to elute in cation-exchange procedures. In some procedures, the process is not quantitative after extensive elution.

SOLVENT EXTRACTION. Cesium does not form many complex ions, and solvent extraction is not a common procedure for its separation. One solvent-extraction procedure, however, is based on chelation of cesium with 1,1,1-trifluoro-3-(2′-thenoyl)acetone (TTA) in a solvent of methyl nitrate/hydrocarbons. Cesium can also be extracted from fission product solutions with sodium tetraphenylborate in amyl acetate. It can be stripped from the organic phase by 3 M HCl.

Methods of Analysis

Macroscopic quantities of cesium have been determined by gravimetric procedures using one of the precipitating agents described above. Spectrochemical procedures for macroscopic quantities include flame photometry, emission spectroscopy, and X-ray emission.

Gamma ray spectrometry allows detection of ^{134}Cs, ^{136}Cs, and ^{137}Cs down to very low levels. The gamma ray measured for ^{137}Cs (661 Kev) actually is emitted from it progeny ^{136m}Ba. However, since the half-life of the barium isotope is so short (2.5 min) it is quickly equilibrated with its

parent cesium isotope (i.e., secular equilibrium). ^{137}Cs is used as part of a group of nuclides in a mixed radioactivity source for calibration of gamma ray spectrometers.

Compiled from: Choppin et al., 1995; Considine and Considine, 1983; Cotton and Wilkinson, 1988; Emsley, 1989; EPA, 1973; EPA, 1973; EPA, 1980; Finston and Kinsley, 1961; Friedlander et al., 1981; Hampel, 1968; Hassinsky and Adolff, 1965; Kallmann, 1964; Lindsay, 1988; Sittig, 1994.

14.10.9.3 Cobalt

Cobalt, atomic number 27, is a silvery-grey, brittle metal found in the first row of the transition elements in the periodic table, between iron and nickel. Although it is in the same family of elements as rhodium and iridium, it resembles iron and nickel in its free and combined states.

Isotopes

^{59}Co is the only naturally occurring isotope of the element. The other twenty-two isotopes and their metastable states, ranging from mass numbers 50 to 67, are radioactive. Isotopes with mass numbers less than 59 decay by positron emission or electron capture. Isotopes with mass numbers greater than 59 decay by beta and gamma emission. Except for ^{60}Co, the most important radionuclide, their half-lives range from milliseconds to days. The principle isotopes of cobalt (with their half-lives) are ^{57}Co (272 d), ^{58}Co (71 d), and ^{60}Co (5.27 y). Isotopes 57 and 58 can be determined by X-ray as well as gamma spectrometry. Isotope 60 is easily determined by gamma spectrometry.

Occurrence and Uses

The cobalt content of the crust of the earth is about 30 ppm, but the element is widely distributed in nature, found in soils, water, plants and animals, meteorites, stars, and lunar rocks. Over 200 cobalt minerals are known. Commercially, the most important are the arsenides, oxides, and sulfides. Important commercial sources also include ores of iron, nickel, copper, silver, manganese, and zinc. ^{60}Co is produced by neutron activation of stable ^{59}Co. ^{56}Co and ^{57}Co are prepared by bombardment of iron or nickel with protons or deuterons.

Some of the metallic cobalt is isolated from its minerals, but much of the metal is produced primarily as a byproduct of copper, nickel, or lead extraction. The processes are varied and complicated because of the similar chemical nature of cobalt and the associated metals.

Since ancient times cobalt ores has been used to produce the blue color in pottery, glass, and ceramics. Cobalt compounds are similarly used as artist pigments, inks, cotton dyes, and to speed the drying of paints and inks. They also serves as catalysts in the chemical industry and for oxidation of carbon monoxide in catalytic converters. One of the major uses of cobalt is the preparation of high-temperature or magnetic alloys. Jet engines and gas turbines are manufactured from metals with a high content of cobalt (up to 65 percent) alloyed with nickel, chromium, molybdenum, tungsten, and other metals.

Little use if made of pure cobalt except as a source of radioactivity from ^{60}Co. The radionuclide is used in cancer radiotherapy, as a high-energy gamma source for the radiography of metallic objects, fluids, and other solids, or as an injectable radionuclide for the measurement of flow rates in pipes.

Solubility of Compounds

Most simple cobalt compounds contain cobalt (II), but cobalt (II) and cobalt(III) display varied solubilities in water. To some extent, their solubilities depend on the oxidation state of the metal. For example, all the halides of cobalt (II) are soluble but the only stable halide of cobalt (III), the fluoride, is insoluble. The sulfates of both oxidation states are soluble in water. The acetate of cobalt (II) is soluble, but that of cobalt (III) hydrolyses in water. The bromate, chlorate, and perchlorate of cobalt (II) are also soluble. Insoluble compounds include all the oxides of both oxidation states, cobalt (II) sulfide, cyanide, oxalate, chromate, and carbonate. The hydroxides are slightly soluble. Several thousand complex compounds of cobalt are known. Almost all are cobalt (III) complexes and many are soluble in water.

Review of Properties

Metallic cobalt is less reactive than iron and is unreactive with water or oxygen in air unless heated, although the finely divided metal is pyrophoric in air. On heating in air it forms the oxides, cobalt (II) oxide (CoO) below 200 °C and above 900 °C and cobalt (II)-cobalt (III) oxide (Co_3O_4) between the temperatures. It reacts with common mineral acids and slowly with hydrofluoric and phosphoric acids to form cobalt (II) salts and with sodium and ammonium hydroxides. On heating, it reacts with halogens and other nonmetals such as boron, carbon, phosphorus, arsenic, antimony, and sulfur.

Cobalt exists in all oxidation states from -1 to +4. The most common are the +2 and +3 oxidation states. The +1 state is found in a several complex compounds, primarily the nitrosyl and carbonyl complexes and certain organic complexes. The +4 state exist in some fluoride complexes.

Cobalt(II) is more stable in simple compounds and is not easily hydrolyzed. Few simple compounds are known for the +3 state, but cobalt is unique in the numerous stable complex compounds it forms.

The toxicity of cobalt is not comparable to metals such as mercury, cadmium, or lead. Inhalation of fine metallic dust can cause irritation of the respiratory system, and cobalt salts can cause benign dermatosis. ^{60}Co is made available in various forms, in sealed aluminum or monel cylinders for industrial applications, as wires or needles for medical treatment, and in various solid and solution forms for industry and research. Extreme care is required in handling any of these forms of cobalt because of the high-energy gamma radiation from the source.

Solution Chemistry

In aqueous solution and in the absence of complexing agents, cobalt (II) is the only stable oxidation state, existing in water as the pink-red hexaaquo complex ion, $Co(H_2O)_6^{+2}$. Simple cobalt ions in the +3 oxidation state decompose water in an oxidization-reduction process that generates cobalt (II):

$$4\ Co^{+3} + 2\ H_2O \rightarrow 4\ Co^{+2} + O_2 + 4\ H^{+1}$$

Complexation of cobalt (III) decreases its oxidizing power and most complex ions of the +3 oxidation state are stable in solution.

COMPLEXATION. Several thousand complexes of cobalt have been prepared and extensively studied, including neutral structures and those containing complex cations and/or anions. Among these, the cobalt (III) complexes are the strongest and represent one of the largest groups of complex compounds. The most common cobalt (III) compounds contain six ligands bonded to the metal atom or cation (coordination number six) in an octahedral arrangement. It forms many complex ions with nitrogen-compounds such as ammonia and amines ($[Co(NH_3)_6]Cl_3$) by coordinating through the nitrogen atom, and with those containing carbon ($K_3[Co(CN)_6]$), oxygen and sulfur ($[Co(H_2O)_6]Cl_3$), and halides ($Na_3[CoF_6]$). Complex compounds with mixed ligands are common: $[Co(NH_3)_5(H_2O)]Cl_3$ and $[Co(NH_3)_3Cl_3]$.

The +2 oxidation state forms complexes with a coordination of four or six, and in aqueous solution, $[Co(H_2O)_6]^{+2}$ is in equilibrium with some $[Co(H_2O)_4]^{+2}$. In alkaline solution Co^{+2} precipitates as $Co(OH)_2$, but the ion is amphoteric; and in concentrated hydroxide solutions, the precipitate dissolves forming $[Co(OH)_4]^{-2}$. Many complexes of the form $[Co(X)_4]^{-1}$ exist with monodentate anionic ligands such as Cl^{-1}, Br^{-1}, I^{-1}, SCN^{-1}, N_3^{-1}, and OH^{-1}. Many aquo-halo

complexes are known; they are various shades of red and blue. The aquo complex, $[Co(H_2O)_6]^{+2}$, is pink.

Chelate complexes are well-known and are used to extract cobalt from solutions of other ions. Acetylacetone (acac) is used, for example, in a procedure to separate cobalt from nickel. Co^{+2} and Ni^{+2} do not form chelates with the acac, Co^{+3} does, however, and can be easily extracted.

OXIDATION-REDUCTION BEHAVIOR. Most simple cobalt +3 compounds are unstable because the +3 state is a strong oxidizing agent. It is very unstable in aqueous media, rapidly reducing to the +2 state at room temperature. The aqueous ion of cobalt(II), $[Co(H_2O)_6]^{+2}$, can be oxidized, however, to the +3 state either by electrolysis or by ozone (O_3) in cold perchloric acid ($HClO_4$); solutions at 0 °C have a half-life of about one week. Compounds of the cobalt(III) complex ions are formed by oxidizing the +2 ion in solution with oxygen or hydrogen peroxide (H_2O_2) in the presence of ligands. The cobalt(III) hexamine complex forms according to:

$$4\ CoX_2 + 4\ NH_4X + 20\ NH_3 + O_2 \rightleftharpoons 4\ [Co(NH_3)_6]X_3 + 2\ H_2O$$

HYDROLYSIS. The hydrolysis of the +2 oxidation state of cobalt is not significant in aqueous media below pH 7. At pH 7, hydrolysis of 0.001 M solution of the cation begins and is significant at a pH above 9. The hydrolysis of the +3 oxidation state is reminiscent of the hydrolysis of iron (III), but it is not as extensive. Hydrolysis of cobalt (III) is significant at pH 5. In contrast, the hydrolysis of iron (III) becomes significant at a pH of about 3.

Dissolution of Samples

Cobalt minerals, ores, metals, and alloys can be dissolved by treatment first with hydrochloric acid, followed by nitric acid. The insoluble residue remaining after application of this process is fused with potassium pyrosulfate and sodium carbonate. In extreme cases, sodium peroxide fusion is used. Biological samples are dissolved by wet ashing, digesting with heating in a sulfuric-perchloric-nitric acid mixture.

Separation Methods

PRECIPITATION AND COPRECIPITATION. Cobalt can be precipitated by hydrogen sulfide (H_2S), ammonium sulfide (NH_4S), basic acetate ($C_2H_3O_2^{-1}/HO^{-1}$), barium carbonate ($BaCO_3$), zinc oxide (ZnO), potassium hydroxide and bromine (KOH/Br_2), ether and hydrochloric acid [$(C_2H_5)_2O$ and HCl], and cupferron. Cobalt sulfide (CoS) is coprecipitated with stannic sulfide (SnS_2) when

low-solubility sulfides are precipitated in mineral acids. Care should be taken to avoid coprecipitation of zinc sulfide (ZnS).

Cobalt can be separated from other metals by hydroxide precipitation using pH control to selectively precipitate metals such as chromium, zinc, uranium, aluminum, tin, iron (+3), zirconium, and titanium at low pH. Cobalt precipitates at pH 6.8, and magnesium, mercury, manganese, and silver at a pH greater than 7. Cobalt is not be separated from metals such as iron, aluminum, titanium, zirconium, thorium, copper, and nickel using ammonium hydroxide (NH_4OH) solutions (aqueous ammonia), because an appreciable amount of cobalt is retained by the hydroxide precipitates of these metals produced using this precipitating agent. Various precipitating agents can be used to remove interfering ions prior to precipitating cobalt: iron by precipitating with sodium phosphate (Na_3PO_4) or iron, aluminum, titanium, and zirconium with zinc oxide.

The separation of cobalt from interfering ions can be achieved by the quantitative precipitation of cobalt with excess potassium nitrite (KNO_2) to produce $K_3[Co(NO_2)_6]$ (caution -- unstable to heating after standing for some time). Ignition can be used to collect the cobalt as its mixed oxide (Co_3O_4). Cobalt can also be precipitated with α-nitroso-β-napthol (1-nitroso-2-napthol) to separate it form interfering metals. Nickel can interfere with this precipitation, but can be removed with dimethylglyoxime. Precipitation as mercury tetracyanatocobaltate (II) $\{Hg[Co(SCN)_4]\}$ also is used, particularly for gravimetric analysis, and precipitation with pyridine in thiocyanate solution is a quick gravimetric product, $[Co(C_5H_5N)_4](SCN)_2$.

SOLVENT EXTRACTION. Various ions or chelates have been used in solvent extraction systems to isolate cobalt from other metals. Separation has been achieved by extracting either cobalt itself or, conversely, extracting contaminating ions into an organic solvent in the presence of hydrofluoric acid (HF), hydrochloric acid, and calcium chloride ($HCl/CaCl_2$), hydrobromic acid (HBr), hydroiodic acid (HI), or ammonium thiocyanate (NH_4SCN). For example, cobalt (II) has been separated from nickel (II) by extracting a hydrochloric acid solution containing calcium chloride with 2-octanol. The ion is not extracted by diethyl ether from hydrobromic acid solutions, but it is extracted from ammonium thiocyanate solutions by oxygen-containing organic solvents in the presence of iron (III) by first masking the iron with citrate.

Several chelate compounds have been used to extract cobalt from aqueous solutions. Acetylacetone (acac) forms a chelate with cobalt (III), but not cobalt (II), that is soluble in chloroform at pH 6 to 9, permitting separation from several metals including nickel. Cobalt (II) can be oxidized to cobalt (III) with hydrogen peroxide (H_2O_2) prior to extraction. α-nitroso-β-napthol has also been used as a chelating agent in the separation of cobalt (III) by solvent

extraction. Diphenylthiocarbazone (dithiozone) has been used at pH 8 to extract cobalt into carbon tetrachloride and chloroform after metals that form dithiozonates in acid solution (pH 3-4) have been removed. 8-quinolinol has been used in a similar manner at pH up to 10. Masking agents added to the system impede the extraction of iron, copper, and nickel.

ION-EXCHANGE CHROMATOGRAPHY. Anion-exchange resins have been used extensively to separate cobalt from other metals. The chloro-metal complexes, prepared and added to columns in molar hydrochloric acid solutions, are eluted at varying concentrations of hydrochloric acid. Trace amounts of ^{59}Fe, ^{60}Co, and ^{65}Zn and their respective carriers have been separated from neutron-irradiated biological tissue ash with a chloride system. ^{60}Co has been eluted carrier-free from similar samples and columns prepared with hydrobromic acid. Cobalt and contaminated metals in nitric-acid systems behave in a manner similar to hydrochloric-acid systems. Cobalt (II)-cyanide and cyanate complexes have been used to separate cobalt from nickel. The basic form of quaternary amine resins (the neutral amine form) has been used in the column chromatography of cobalt. Both chloride- and nitrate-ion systems have resulted in the association of cobalt as a complex containing chloride or nitrate ligands as well as the neutral (basic) nitrogen atom of the amine resin. Resins incorporating chelates in their matrix system have been used to isolate cobalt. 8-quinolinol resins are very effective in separating cobalt from copper.

ABSORBENT CHROMATOGRAPHY. Several inorganic adsorbents such as alumina, clays, and silica are used to separate cobalt. Complex ions of cobaltamines separate on alumina as well as cobalt (II) complexes of tartaric acid and dioxane. A complex of nitroso-R-salts are absorbed onto an alumina column while other metals pass through the column. Cobalt is eluted with sulfuric acid. Cobalt dithizonates absorb on alumina from carbon tetrachloride solutions. Cobalt is eluted with acetone. The separation of cobalt from iron and copper has been achieved on aluminum hydroxide [$Al(OH)_3$]. Clay materials, kalolinite, benotite, and montmorilloite, separate cobalt (II) from copper (II). Copper (II) absorbs and cobalt (II) elutes with water. Silica gel and activated silica have both been used as adsorbents in cobalt chromatography.

Organic adsorbents such as 8-hydroxyquinoline and dimethylgloxime have been used in cobalt-absorbent chromatographic systems. Powdered 8-hydroxyquinoline separates cobalt (II) from other cations and anions, for example, and dimethylglyoxime separates cobalt from nickel. Cobalt-cyano complexes absorb on activated charcoal, and cobalt is eluted from the column while the anionic complexes of metals such as iron, mercury, copper, and cadmium remain on the column.

Numerous paper chromatograph systems employing inorganic or chelating ligands in water or organic solvents are available to separate cobalt from other metals. In one system, carrier-free

^{60}Co and ^{59}Fe from an irradiated manganese target were separated with an acetone-hydrochloric solvent.

ELECTRODEPOSTION. Most electroanalytical methods for cobalt are preceded by isolating the cobalt from interfering ions by precipitation or ion exchange. The electrolyte is usually an ammonia solution that produces the hexamine complex of cobalt (II), $Co(NH_3)_6^{+2}$ in solution. Reducing agents such as hydrazine sulfate are added to prevent anodic deposits of cobalt and the oxidation of the cobalt (II)-amine ion. Cobalt and nickel can be separated electrolytically by using an aqueous solution of pyridine with hydrazine to depolarize the platinum anode. The nickel is deposited first, and the voltage is increased to deposit cobalt.

Methods of Analysis

^{57}Co, ^{58}Co, and ^{60}Co maybe concentrated from solution by coprecipitation and determined by gamma-ray spectrometry. ^{60}Co is most commonly produced by the neutron activation of ^{59}Co, in a reactor or an accelerator. ^{58}Co is most commonly produced from the following reaction in nuclear reactors, $^{58}Ni(n,p)^{58}Co$, due to the presence of nickel bearing alloys which undergo corrosion and are transported through the reactor core. ^{58}Co is the most significant contributor to the gamma ray induced radiation fields in these facilities. ^{57}Co can be produced by either of the following, $^{58}Ni(n,d)^{57}Co$ [reactor] or $^{56}Fe(d,n)^{57}Co$ [accelerator], ^{57}Co and ^{60}Co are frequently used as part of a mixed radionuclide source for calibration of gamma ray spectrometers.

Compiled from: Baes and Mesmer, 1976; Bate and Leddicotte, 1961; Cotton and Wilkinson, 1988; Dale and Banks, 1962; EPA, 1973; Greenwood and Earnshaw, 1984; Haissinsky and Adloff, 1965; Hillebrand et al., 1980; Larsen, 1965; Latimer, 1952; Lingane, 1966.

14.10.9.4 Iodine

Iodine is a nonmetal, the last naturally occurring member of the halogen series, with an atomic number of 53. In the elemental form it is a diatomic molecule, I_2, but it commonly exists in one of four nonzero oxidation states: -1 with metal ions or hydrogen; and +1, +5, and +7 with other nonmetals, often oxygen. Numerous inorganic and organic compounds of iodine exist, exhibiting the multiple oxidation states and wide range of physical and chemical properties of the element and its compounds. Existence of multiple oxidation states and the relative ease of changing between the -1, 0, and +5 state allows readily available methods for separation and purification of radionuclides of iodine in radiochemical procedures.

3867 Isotopes

3868 There are 42 known isotopes of iodine, including seven metastable states. The mass numbers
3869 range from 108 to 142. The only stable isotope is naturally occurring ^{127}I. The half-lives of the
3870 radionuclides range from milliseconds to days with the single exception of long-lived ^{129}I
3871 ($t_{1/2}$=1.57 x 10^7 y). Iodine radionuclides with lower mass numbers decay primarily by electron
3872 capture. The higher mass number are, for the most part, beta emitters. The significant
3873 radionuclides are ^{125}I ($t_{1/2}$=60.1d, electron capture), ^{129}I (beta), and ^{131}I ($t_{1/2}$=8.0d, beta).

3874 Occurrence and Uses

3875 Iodine is widely distributed, but never found in the elemental form. The average concentration in
3876 the earth's crust is about 0.3 ppm. In seawater, iodine concentration, in the form of sodium or
3877 potassium iodide, is low (about 50 ppb), but it is concentrated in certain seaweed, especially kelp.
3878 It is also found in brackish waters from oil and salt wells. The sources are saltpeter and nitrate-
3879 bearing earth in the form of calcium iodate, well brine, and seaweed. Iodine is produced from
3880 calcium iodate by extraction of the iodate from the source with water and reduction of the iodate
3881 with sodium bisulfite to iodine. Iodine is precipitated by mixing with the original iodate liquor to
3882 cause precipitation. Iodine can also be obtained from well brine, where the iodide ion is oxidized
3883 with chlorine, and then the volatile iodine is blown out with a stream of air. Sodium or potassium
3884 iodide in seaweed is calcined to an ash with sulfuric acid, which oxidizes the iodide to iodine.
3885 Iodine from any of these processes can be purified by sublimation.

3886 Isotopes of iodine of mass ≥ 128 may all be formed as a result of fission of uranium and
3887 plutonium. Nuclear reactors and bomb tests are the most significant sources of these radioiso-
3888 topes with the exception of ^{131}I. That isotope is routinely produced for use in medical imaging
3889 and diagnosis. The isotopes released from the other sources represent a short term environmental
3890 health hazard should there be an abnormal release from reactors or if bomb testing or use were to
3891 occur.

3892 This was the case in both 1979 and 1986 when the power reactor events at Three Mile Island and
3893 Chernobyl, caused releases of radioiodines. During the former event a ban on milk distribution in
3894 the downwind corridor was enforced as a purely preventative measure. In the latter case, signifi-
3895 cant releases of iodines and other isotopes caused more drastic, long term measures for food
3896 quarantine.

3897 Deposits on the surface of plants could provide a quick source of exposure if consumed directly
3898 from fruits and vegetables or indirectly from cow's milk. It would readily accumulate in the

thyroid gland, causing a short-term exposure of concern. It represent the greatest short-term exposure after a nuclear detonation and has been released in power plant accidents. ^{129}I, with of a half-life of more than 15 million years, represent a long-term environmental hazard. In addition to its long half-life, the environmental forms of iodine in the environment are highly soluble in groundwater and are poorly sorbed by soil components. It is not absorbed at all by granite, and studies at a salt repository indicate that ^{129}I would be only one of few radionuclides that would reach the surface before it decayed. Therefore, research on the fate of ^{129}I that might be released suggests that the radionuclide would be highly disseminated in the ecosystem.

^{131}I is routinely analyzed for in milk, soil and water. ^{129}I is a low energy beta and gamma emitter, which has a very long half-life (1.47×10^7 years). The most significant concern for this isotope is in radioactive waste, and its potential for migration due to the chemistry of iodine in the environment. ^{131}I is produced for medical purposes by neutron reaction as follows: $^{130}Te(n,\gamma)^{131}Te$ → beta decay → ^{131}I (half-life = 8 days).

The major use of iodine, iodine radionuclides, and iodine compounds is in medical diagnosis and treatment. ^{123}I, ^{125}I, and ^{131}I are use for diagnostic imaging of the thyroid gland and the kidneys. ^{131}I is used to treat hyperthyroidism and thyroid cancer. Stable iodine in the form of potassium iodide is added to commercial salt to prevent enlargement of the thyroid (goiter). Iodine in the form of the hormone thyroxine is also used for thyroid and cardiac treatment and hormone replacement therapy in iodine deficiency. Iodine radionuclides are used as a tracer in the laboratory and industry to study chemistry mechanisms and processes and to study biological activity and processes. Iodine is a bactericide and is used as an antiseptic and sterilization of drinking water. It is used as a catalyst in chemical processes and as silver iodide in film emulsions.

Solubility of Compounds

Molecular iodine is only very slightly soluble in water (0.33 g/L), but it is soluble in solutions of iodide ion, forming I_3^{-1}. It is appreciably soluble in organic solvents. Carbon tetrachloride (CCl_4) or chloroform ($CHCl_3$) are commonly used to extract iodine from aqueous solutions after alternate forms of the element, typically I^{-1} and IO_3^{-1}, are converted to I_2. The solutions have a violet color in organic solvents, and iodine dimerizes to some extent in these solutions:

$$2\ I_2 \rightleftharpoons I_4$$

Numerous compounds of iodine are soluble in water. All metallic iodides are soluble in water except those of silver, mercury, lead, cupurous ion, thallium, and palladium. Antimony, bismuth,

and tin iodides require a small amount of acid to keep them in solution. Most of the iodates and periodates are insoluble. The iodates of sodium, potassium, rubidium, and the ammonium ion are soluble in water. Those of cesium, cobaltous ion, magnesium, strontium, and barium are slightly soluble in water but soluble in hot water. Most other metallic iodates are insoluble.

Review of Properties

Elemental iodine (I_2) is a purple-black, lustrous solid at room temperature with a density of 4.9 g/cm^3. The brittle crystals have a slightly metallic appearance. Iodine readily sublimes and stored in a closed clear, colorless container, it produces a violet vapor with an irritating odor. Iodine has a melting point of 114 °C and a boiling point of 184 °C.

The chemical reactivity of iodine is similar to the other halogens, but it is the least electronegative member of the family of elements and the least reactive. It readily reduces to iodide, and is displaced from its iodides by the other halogens and many oxidizing agents. Iodine combines directly with most elements to form a large number of ionic and covalent compounds. The exceptions are the noble gases, carbon, nitrogen, and some noble metals.

The inorganic compounds of iodine can be classified into three groups: (1) iodides, (2) interhalogen, and (3) oxides. Iodine forms iodides that range from ionic compounds such as potassium iodide (KI) to covalent compounds such as titanium tetraiodide (TiI_4) and phosphorus triiodide (PI_3), depending on the identity of the combining element. More electropositive (less electronegative) metals (on the left side of the periodic table, such as alkali metals and alkaline earths) form ionic compounds. Less electropositive metals and more electronegative nonmetals tend to form covalent compounds. Interhalogen compounds include the binary halides, such as iodine chloride (ICl), iodine trichloride (ICl_3), and iodine pentafluoride (IF_5), or contain interhalogen cations and anions, such as ICl_2^{+1}, IF_6^{+1}. I^{+3}, $ClIBr^{-1}$, ICl_4^{-1}, and I_6^{-2}. Oxygen compounds constitute the oxides, I_2O_5 and I_4O_9 (containing one I^{+3} cation and three IO_3^{-1} anions), for example; the oxyacids, such as hypoiodous acid (HIO) and iodic acid (HIO_3); and compounds containing oxyanions, iodates (IO_3^{-1}) and periodates (IO_4^{-1}) are the common ones.

Organoiodides include two categories: (1) iodides and (2) iodide derivatives with iodine in a positive oxidation state because iodine is covalently bonded to another, more electronegative element. Organoiodides contain a carbon iodide bond. They are relatively dense and volatile and more reactive than the other organohalides. They include the iodoalkanes such as ethyl iodide (C_2H_5I) and iodobenzene (C_6H_5I). Dimethyliodonium (III) hexafluoroantimonate [$(CH_3)_2I^{+3}SbF_6^{-3}$], a powerful methylating agent, is an example of the second category.

The toxicity of molecular iodine is primarily related to its vapor state and to solutions. Iodine vapor is an eye and nasal irritant, potentially causing damage to the eyes and serious respiratory damage. Solid iodine is not a serious problem unless confined to the skin where it causes discoloration and eventually burns. Solutions of iodine are toxic if taken internally. The radionuclides of iodine are radiotoxic, primarily because of their concentration in the thyroid gland. Radiotoxicity of ^{129}I, if released, is a concern because of its extremely long half-life. ^{131}I, with a half-life of eight days, is a short-term concern. The whole-body effective biological half-lives of ^{129}I and ^{131}I are 140 d and 7.6 d, respectively.

Solution Chemistry

OXIDATION-REDUCTION BEHAVIOR. Iodine can exist in multiple oxidation states in solution, but the radiochemist can control the states by selection of appropriate oxidizing and reducing agents. In acid and alkaline solutions, the common forms of iodine are: I^{-1}, I_2, and IO_3^{-1}. Hypoiodous acid (HIO) and the hypoiodite ion (IO^{-1}) can form in solution, but they rapidly disproportionate:

$$5\ HIO \rightleftharpoons 2\ I_2 + IO_3^{-1} + H^{+1} + 2\ H_2O$$

$$3\ IO^{-1} \rightleftharpoons 2\ I^{-1} + IO_3^{-1}$$

Iodine itself is not a powerful oxidizing agent, less than that of the other halogens (F_2, Cl_2, and Br_2), but its action is generally rapid. Several oxidizing and reducing agents are used to convert iodine into desired oxidation states during radiochemical procedures. These agents are used to promote radiochemical equilibrium between the analyte and the carrier or tracer or to produce a specific oxidation state before separation: I_2 before extraction in an organic solvent or I^{-1} before precipitation, as examples. Table 14.19 presents oxidizing and reducing agents commonly used in radiochemical procedures:

Table 14.19 — Common radiochemical oxidizing and reducing agents for iodine

Redox Process	Redox Reagent	Notes
$I^{-1} - I_2$	HNO_2 ($NaNO_2$ in acid)	Does not affect other halides
$I^{-1} - IO_3^{-1}$	MnO_2 in acid	Well suited for laboratory work
$I_2 - I^-$	6 M HNO_3 $NaHSO_3$ and $NaHSO_4$ (in acid) Na_2SO_3 and $Na_2S_2O_3$ $Fe_2(SO_4)_3$ (in acid)	
$I^{-1} - IO_4^{-1}$	$KMnO_4$ 50% CrO_3 in 18N H_2SO_4	

Redox Process	Redox Reagent	Notes
$I^{-1} - IO_4^{-1}$	NaClO in base	
$IO_4^{-1} - I_2$	$NH_2OH \cdot HCl$	
$IO_3^{-1} - I_2$	$NH_2OH \cdot HCl$ $H_2C_2O_4$ in 18N H_2SO_4	
$IO_4^{-1} - I^{-1}$	$NaHSO_3$ in acid	
$I_2 - I^{-1}$	SO_2 gas $NaHSO_3$ and $(NH_4)_2SO_3$	

Radiochemical exchange between I_2 and I^{-1} in solution is complete within time of mixing and before separation. In contrast, exchange between I_2 and IO_3^{-1} or IO_4^{-1} in acid solution and between IO_3^{-1} and IO_4^{-1} in acid or alkaline solution is slow. For radiochemical analysis of iodine, experimental evidence indicates that the complete and rapid exchange of radioiodine with carrier iodine can be accomplished by the addition of the latter as I^{-1} and subsequent oxidation to IO_4^{-1} by NaClO in alkaline solution, addition of IO_4^{-1} and reduction to I^{-1} with $NaHSO_3$, or addition of one followed by redox reactions first to one oxidation sate and then back to the original state.

COMPLEXATION. As a nonmetal, iodine is generally not the central atom of a complex, but it can act as a ligand to form complexes such as SiI_6^{-2} and CoI_6^{-3}. An important characteristic of molecular iodine is its ability to combine with the iodide ion to form polyiodide anions. The brown triioide is the most stable:

$$I_2 + I_{-1} \rightleftharpoons I_3^{-1}$$

The equilibrium constant for the reaction in aqueous solution at 25 °C is 725, so appreciable concentrations of the anion can exist in solution, and the reaction is responsible for the solubility of iodine in iodide solutions.

HYDROLYSIS. Iodine hydrolyzes in water through a disproportionation reaction:

$$I_2 + H_2O \rightleftharpoons H^{+1} + I^{-1} + HIO$$

Because of the low solubility of iodine in water and the small equilibrium constant ($k=2.0 \times 10^{-13}$), hydrolysis produces negligible amounts of the products (6.4×10^{-6} M) even when the solution is saturated with iodine. Disproportionation of HIO produces a corresponding minute quantity of IO_3^{-1} (see the reaction above). In contrast, in alkaline solution, I_2 produces I^{-1} and IO^{-1}:

$$I_2 + 2\ OH^{-1} \rightleftharpoons I^{-1} + IO^{-1} + H_2O$$

The equilibrium constant favors the products (k=30), but the actual composition of the solution is complicated by the disproportionation of IO^{-1} (illustrated above), giving I^{-1} and IO_3^{-1}. The equilibrium constant for the reaction of IO^{-1} with hydroxide ion is very large (10^{20}), and the rate of the reaction is very fast at all temperatures. Therefore, the actual products obtained by dissolving iodine in an alkaline solution are indeed I^{-1} and IO_3^{-1}, quantitatively, and IO^{-1} does not exist in the solution.

Dissolution of Samples

Iodine compounds in rocks are often in the form of iodides that are soluble in either water or dilute nitric acid when the finely divided ores are treated with one of these agents. Those that are insoluble under these conditions are solubilized with alkali fusion with sodium carbonate or potassium hydroxide, followed by extraction of the residue with water. Insoluble periodiates can be decomposed by cautious ignition, converting them to soluble iodides.

Metals containing iodine compounds are dissolved in varying concentrations of nitric, sulfuric, or hydrochloric acids. Dissolution can often be accomplished at room temperature or might require moderation in an ice bath.

Organoiodides are decomposed with a sodium peroxide, calcium oxide, or potassium hydroxide by burning in oxygen in a sealed bomb. Wet oxidation with mixtures of sulfuric and chromic acids or with aqueous hydroxide is also used.

Separation Methods

PRECIPITATION. The availability of stable iodine as a carrier and the relative ease of producing the iodide ion make precipitation a simple method of concentrating and recovering iodine radionuclides. The two common precipitating agents are silver (Ag^{+1}) and palladium (II) (Pd^{+2}) cations, which form silver iodide (AgI) and palladium iodide (PdI_2), respectively. Silver iodide can be solubilized with a 30 percent solution of potassium iodide. Palladium precipitates iodide in the presence of chloride and bromide, allowing the separation of iodide from these halides. The precipitating agent should be free of palladium (IV), which will precipitate chloride. If palladium (II) iodide is dried, precaution should be taken as the solid slowly looses iodine if heated at 100 °C. Iodate can be precipitated as silver iodate, and periodate as lead periodate.

SOLVENT EXTRACTION. One solvent extraction method is commonly used to isolate iodine. After preliminary oxidation-reduction steps to insure equilibrium of all iodine in solution, molecular iodine (I_2) is extracted from aqueous solutions by a nonpolar solvent, usually carbon tetrachloride

or chloroform. It is not uncommon to add small quantities of the oxidizing or reducing agent to the extraction solution to ensure and maintain all iodine in the molecular form. Hydroxylamine is added, for example, if iodate is the immediate precursor of iodine before extraction.

ION-EXCHANGE CHROMATOGRAPHY. Both cation and anion exchange procedures are used to separate iodine from contaminants. Cation-exchange chromatography has been used to remove interfering cations. To remove ^{137}Cs activity, an iodine sample in the iodide form is absorbed on a cation-exchange resin and eluted with ammonium sulfite [$(NH_4)_2SO_3$], to ensure maintenance of the iodide form. Cesium cations remain the resin. Bulk resin is also used, and iodide is washed free of the resin as the periodate with sodium hypochlorite (NaClO) as the oxidizing agent. Anion-exchange resins provide absorption of the iodide ion. The halides have been separated from each other on an anion-exchange column prepared in the nitrate form by eluting with 1 M sodium nitrate. Iodide can also be separated from contaminants by addition to an anion exchanger and elution as periodate with sodium hypochlorite. The larger periodate anion is not as strongly attracted to the resin as the iodide ion. ^{131}I separation, collection, and analysis is performed by absorbing the radionuclide on an anion-exchange resin and gamma counting it on the sealed column after eluting the contaminants.

DISTILLATION. Molecular iodine is a relatively volatile substance. Compared to many contaminating substances, particularly metal ions in solution, its boiling point of 184 °C is very low, and the volatility of iodine provides a method for its separation from other substances. After appropriate oxidation-reductions steps to convert all forms of iodine into the molecular form, iodine is distilled from aqueous solution into sodium hydroxide and collected by another separation process, typically solvent extraction. In hydroxide solution, molecular iodine is converted to a mixture of iodide and hypoiodite ions and then into iodide and periodate ions, and suitable treatment is required to convert all forms into a single species for additional procedures.

Methods of Analysis

Macroquantities of iodine can be determined gravimetrically by precipitation as silver iodide or palladium iodide. The latter substance is often used to determine the chemical recovery in radiochemical analyses. Microquantities of ^{129}I and ^{131}I are coprecipitated with palladium iodide using stable iodide as a carrier and counted for quantification. ^{129}I usually is beta counted in a liquid-scintillation system, but it can also be determined by gamma-ray spectrometry. ^{131}I is determined by gamma-ray emission.

Compiled from: Adams, 1995; APHA, 1998; Armstrong et al., 1961; Bailar et al., 1984; Choppin et al., 1995; Considine and Considine, 1983; Cotton and Wilkinson, 1988; DOE,

1990 and 1997, 1997; EPA, 1973; EPA, 1980; Ehmann and Vance, 1991; Greenwood and Earnshaw, 1984; Haissinsky and Adloff, 1965; Kleinberg and Cowan, 1960; Latimer, 1952; Lindsay, 1988.

14.10.9.5 Plutonium

Plutonium, with an atomic number of 94 is an actinide and the second element in the transuranic series. Essentially all plutonium is an artifact, most produced by neutron bombardment of ^{238}U followed by two sequential beta emissions, but trace quantities of plutonium compounds can be found in the natural environment. Plutonium radiochemistry is complicated by the five possible oxidation states that can exist; four can be present in solution at one time.

Isotopes

Plutonium has 18 isotopes with mass numbers ranging from 232 to 247, and all isotopes are radioactive. Some have a long half-life: the isotope of greatest importance, ^{239}Pu, has a half-life of 24,110 years, but ^{242}Pu and ^{244}Pu have a half-lives of 376,000 and 76,000,000 years, respectively. ^{238}Pu, ^{240}Pu, and ^{241}Pu have a half-lives of 87.74, 6,537, and 14.4 years, respectively. Four of these isotopes decay by alpha emission accompanied by weak gamma rays: ^{238}Pu, ^{239}Pu, ^{240}Pu, and ^{242}Pu. In contrast, ^{241}Pu decays by beta emission with weak gamma rays but its progeny is ^{241}Am, an intense gamma emitter. ^{239}Pu and ^{241}Pu are fissile materials—they can be split by both fast and slow neutrons. ^{240}Pu, and ^{242}Pu are fissionable but have very small neutron fission cross-sections. ^{240}Pu partly decays by spontaneous fission, although a small amount of spontaneous fission occurs in most plutonium isotopes.

Occurrence and Uses

There are minute quantities of plutonium compounds in the natural environment as the result of thermal neutron capture and subsequent beta decay of naturally occurring ^{238}U. All plutonium of concern is an artifact, the result of neutron bombardment of uranium in a nuclear reactor. Virtually all nuclear power-plants of all sizes and the waste from the plants contain plutonium because ^{238}U is the main component of fuel used in nuclear reactors. It is also associated with the nuclear weapons industry and its waste. Virtually all the plutonium in environmental samples is found in air samples as the results of atmospheric weapons testing. Plutonium in plant and crop samples is essentially caused by surface absorption.

Plutonium is produced in nuclear reactors from ^{238}U that absorbs neutrons emitted by the fission of ^{235}U, which is a naturally occurring uranium isotope found with ^{238}U. ^{239}U is formed and emits

a beta particle to form ^{239}Np that decays by beta emission to form ^{239}Pu. Once started, the process is spontaneous until the uranium fuel rods become a specific uranium-plutonium mixture. The rods are dissolved in acid, and plutonium is separated primarily by solvent extraction, finally producing a concentrated plutonium solution. Pure plutonium metal can be prepared by precipitating plutonium peroxide or oxalate, igniting the precipitate to PuO_2, converting the oxide to PuF_3, and reducing Pu(III) to the metal in an ignited mixture containing metallic calcium.

Large quantities of ^{239}Pu have been used as the fissile agent in nuclear weapons and as a reactor fuel when mixed with uranium. It is also used to produce radioactive isotopes for research, including the study of breeder reactors, and ^{238}Pu is used as a heat source to power instruments for space exploration and implanted heart pacemakers.

Solubility of Compounds

General solubility characteristics include the insolubility of the hydroxides, fluorides, iodates, phosphates, carbonates, and oxalates of Pu(III) and Pu(IV). Some of these can be dissolved in acid solution, however. The corresponding compounds of PuO_2^{+1} and PuO_2^{+2} are soluble, with the exception of the hydroxides. The binary compounds represented by the carbides, silicides, sulfides, and selenides are of particular interest because of their refractory nature. One of the complicating factors of plutonium chemistry is the formation of a polymeric material by hydrolysis in dilute acid or neutral solutions. The polymeric material can be a complicating factor in radiochemical procedures and be quite unyielding in attempts to destroy it.

Review of Properties

Plutonium metal has some unique physical properties: a large piece is warm to the touch because of the energy produced by alpha decay, and it exists in six allotropic forms below its melting point at atmospheric pressure. Each form has unusual thermal expansion characteristics that prevents the use of unalloyed plutonium metal as a reactor fuel. The delta phase, however, can be stabilized by the addition of aluminum or gallium and be used in reactors. Chemically, plutonium can exist in five oxidation states: III, IV, V, VI, and VII. The first four states can be observed in solution, and solid compounds of all five states have been prepared. The metal is a silver-grey solid that tarnishes in air to form a yellow oxide coating. It is chemically reactive combining directly with the halogens, carbon, nitrogen, and silicon.

Plutonium is a very toxic substance, but outside the body, it does not represent great danger from it low penetrating alpha emission or emission of its low intensity beta, gamma, or neutron radiation. Ingested plutonium is not readily absorbed into the body, but passes through the

digestive tract and expelled before it can cause significant harm. Inhaled plutonium presents a significant danger. Particularly, inhalation of particles smaller than one micron would be a serious threat due to the alpha-emitting radionuclide being in direct contact with lung tissue. Plutonium would also be very dangerous if it were to enter the blood stream through an open wound, because it would concentrate in the liver and bones, leading to damage to the bone marrow and subsequent related problems. For these reasons, plutonium is handled in gloveboxes with associated precautions taken to protect the worker from direct contact with the material. When working with plutonium in any form, precautions should also be taken to prevent the accumulation of quantities of fissionable plutonium that would achieve a critical mass, particularly in solution where it is more likely to become critical than solid plutonium.

Most of the plutonium in the environment is the result of weapons testing. More than 99 percent of the plutonium from these activities was released during atmospheric tests, but a small portion was also released during ground tests. An even smaller quantity is released by nuclear fuel reprocessing plants, some in the ocean, and by nuclear waste repositories. Part of the atmospheric plutonium, originally part of the weapons, settled to the earth as an insoluble oxide, locating in the bottom sediments of lakes, rivers, and oceans or becoming incorporated in sub-surface soils. The majority of environmental plutonium isotopes are the result of atmospheric nuclear bomb tests. If the bomb material is made from uranium, the oxide is enriched to high percentages of ^{235}U, the fissile isotope. The ^{238}U isotope does not fission, but absorbs 1-2 neutrons during the explosion forming isotopes of ^{239}U and ^{240}U. These isotopes beta decay within hours to their neptunium progeny, which in turn decay to ^{239}Pu and ^{240}Pu. Bombs from plutonium would yield higher fractions of $^{240,241,242}Pu$.

Plutonium formed as a result of atmospheric tests is most likely to be in the form of a fine particulate oxide. If as in the case of a low altitude or underground test, there is a soil component, the plutonium will be fused with siliceous minerals. The behavior of the soluble form of plutonium would be similar to that released from fuel reprocessing plants and from nuclear waste sites. Like the insoluble oxide, most of the soluble form is found in sediments and soils, but a small percentage is associated with suspended particles in water. Both the soluble form of plutonium and the form suspended on particulate matter are responsible for plutonium transportation in the environment. Plutonium in soil is found where the humic acid content is high. In non-humic, carbonate-rich soils, plutonium migrates downward. Migration in the former soil is slow ($\leq$0.1 cm/y) and in the latter it is relatively fast (1-10 cm/y). In subsurface oxic soil, plutonium is relatively mobile, transported primarily by colloids. In wet anoxic soils, most of the plutonium is quickly immobilized, although a small fraction remains mobile. The average time plutonium remains in water is proportional to the amount of suspended material. For this reason, more than

90 percent of plutonium is removed from costal water, while the residence time in mid-ocean water where particulate matter is less is much longer.

Solution Chemistry

The equilibration problems of plutonium are among the most complex encountered in radiochemistry. Plutonium can form five oxidation states in solution, +3, +4, +5, +6, and +7. The first four are present in solution as Pu^{+3}, Pu^{+4}, PuO_2^{+1}, PuO_2^{+2}. They coexist in dilute acid solution, and sometimes all four are present in substantial quantities. Problems of disproportionation and auto-oxidation in freshly prepared solutions also complicate the chemistry of plutonium. The +7 state can form in alkaline solutions, and it has been suggested that the ion in solution is PuO_5^{-3}. Plutonium ions tend to hydrolyze and form complex ions in solution. The +4 ion can form long chain polymers that do not exhibit the usual chemical behavior of the +4 oxidation state. Finally, the different oxidation states exhibit radically different chemical behavior. As a result of these effects, it is possible to mix a plutonium sample with plutonium tracer, subject the mixture to a relatively severe chemical treatment using hot acids or similar reagents, and still selectively recover portions of either the tracer or the sample. This characteristic explains the challenge in achieving reproducible radiochemical results for plutonium.

OXIDATION-REDUCTION BEHAVIOR. Numerous redox agents are available to oxidize and reduce any of the five states of plutonium to alternate oxidation states. The following table provides a convenient method of preparation of each state and illustrates the use of redox reagents in plutonium chemistry:

Table 14.20 — Redox agents in plutonium chemistry

Oxidation State	Form	Method of Preparation
III	Pu^{+3}	Dissolve Pu metal in HCl and reduce Pu^{+4} with NH_2OH, N_2H_4, SO_2, or by cathodic reduction
IV	Pu^{+4}	Oxidize Pu^{+3} with hot HNO_3; treat Pu^{+3} or PuO_2^{+2} with NO_2^{-1}
IV	$PuO_2 \cdot nH_2O$ (polymer)	Heat Pu^{+4} in very dilute acid; peptize $Pu(OH)_4$
V	PuO_2^{+1}	Reduce PuO_2^{+2} with stoichiometric amount of I^{-1} or ascorbic acid; electrolytic reduction of PuO_2^{+2}
VI	PuO_2^{+2}	Oxidize Pu^{+4} with hot dilute HNO_3 or AgO; ozonize Pu^{+4} in cold dilute HNO_3 with Ce^{+3} or Ag^{+1} catalyst
VII	PuO_5^{-3} (?)	Oxidize PuO_2^{+2} in alkali with O_3, $S_2O_8^{-2}$ or radiation

Unlike uranium, the +3 oxidation state is stable enough in solution to be useful in separation chemistry. Disproportionation reactions convert Pu^{+4} to Pu^{+3} and PuO_2^{+2} releasing H^{+1}. The presence of acid in the solution or complexing agents represses the process. Similarly, PuO_2^{+1} disproportionates producing the same products but with the consumption of H^{+1}. For this reason, PuO_2^{+1} is not predominant in acid solutions. These disproportionation reactions can be involved in redox reactions by other reagents. Instead of direct oxidation or reduction, the disproportionation reaction can occur first, followed by direct oxidation or reduction of one of the products.

It is possible to prepare stable aqueous solutions in which appreciable concentrations of the first four oxidation states exist simultaneously: the +3, +4, +5, and +6 states. The relative proportions of the different oxidation states depend on the acid, the acid concentration, the method of preparation of the solution, and the initial concentrations of each of the oxidation states. These relative concentrations will change over time and ultimately establish an equilibrium specific to the solution. In 0.5 M HCl at 25 °C, for example, the equilibrium percentages of the four oxidation states prepared from initially pure Pu^{+4} are +3 (27.2%), +4 (58.4%), +5 (0.7%), and +6 (13.6%). Freshly prepared plutonium samples are frequently in the +4 state, while an appreciable amount of the +3 and +6 oxidation states will be present in long-standing tracer solutions.

A convenient solution to this plutonium equilibration problem takes the form of a two step process:

- boil the combined sample and tracer with a concentrated inorganic acid (e.g., HNO_3) to destroy any +4 polymers that might have formed, and

- cool and dilute the solution; then rapidly (to avoid reforming polymers) treat the solution with excess iodide ion (solution turns brown or black) to momentarily reduce all of the plutonium to the +3 oxidation state.

The solution will immediately start to disproportionate in the acid medium, but the plutonium will have achieved a true equilibrium starting at a certain time from one state in the solution.

Alpha particles emitted by ^{239}Pu can decompose solutions of the radionuclide by radiolysis. The radiolysis products then oxidize or reduce the plutonium, depending on the nature of the solution and the oxidation state of the element. The nature of the anion present greatly influences the rate of the redox process. For the radiochemist it is important to recognize that for old plutonium solutions, particularly those in low acidity, the oxidation labeled states are not reliable.

HYDROLYSIS AND POLYMERIZATION. Hydrolysis is most pronounced for relatively small and highly charged ions such as Pu^{+4}, but plutonium ions in any oxidation state are more easily hydrolyzed than their larger neptunium and uranium analogues.

Trivalent plutonium tends to hydrolyze more than neptunium or uranium, but the study of its hydrolysis characteristics has been hindered by precipitation, formation of Pu^{+4}, and unknown polymerization. In strongly alkaline solutions, $Pu(OH)_3$ precipitates; the solubility product constant is estimated to be 2×10^{-20}.

Plutonium(IV) exists as a hydrated ion in solutions that are more acidic than 0.3 M H^{+1}. Below 0.3 M, it undergoes much more extensive hydrolysis than any other plutonium species, or at lower acidities (0.1 M) if the plutonium concentration is lower. Thus, the start of hydrolysis depends on the acid/plutonium ratio as well as the temperature and presence of other ions. On hydrolysis, only $Pu(OH)^{+3}$ is important in the initial phases, but it tends to undergo irreversible polymerization, forming polymers with molecular weights as high as 10^{10} and chemical properties much different from the free ion. Presence of the polymer can be detected by its bright green color. When plutonium (IV) hydroxide [$Pu(OH)_4$] is dissolved in dilute acid, the polymer also forms. Similarly, if a solution of Pu^{+4} in moderately concentrated acid is poured slowly into boiling water, extensive polymerization occurs. The colloidal character of the polymer is manifested by its strong adsorption onto glass, silica, or small bits of paper or dirt. The chemical characteristics of the polymer, with regard to precipitation, ion-exchange, and solvent extraction, is markedly different than the chemistry of the common +4 oxidation state of plutonium. Care should be taken in the laboratory to avoid the formation of these polymers. For instance, these polymers can be formed by overheating solutions during evaporation. Moreover, diluting an acidic plutonium solution with water can cause polymerization because of localized areas of low acidity, even when the final concentration of the solution is too high for polymerization. Therefore, plutonium solutions should always be diluted with acid rather than water. Polymeric plutonium can also be formed if insufficient acid is used when dissolving plutonium (IV) hydroxide.

Immediately after formation, these polymers are easy to decompose by acidification with practically any concentrated inorganic acid or by oxidation. Because depolymerization is slow at room temperature and moderate acid concentrations, solutions should be made at least 6 M and boiled to destroy the polymers. The polymer is rapidly destroyed under these conditions. Adding strong complexing agents such as fluoride, sulfate, or other strong complexing agents can increase the rate of depolymerization. However, if the polymers are allowed to "age," they can be very difficult to destroy.

The PuO_2^{+1} ion has only a slight tendency to hydrolyze, beginning at pH 8, but study of the extent of the process is inhibited by the rapid disproportionation of hydrolyzed plutonium(V).

Hydrolysis of PuO_2^{+2} is far more extensive than expected for a large +2 ion. Hydrolysis begins at pH of about 2.7 to 3.3, giving an orange color to the solution that yields to bright yellow by pH 5. Between pH 5 and 7, dimerizatons seem to occur, and by pH 13 several forms of plutonium hydroxide have been precipitated with solubility products of approximately 2.5×10^{-25}.

COMPLEXATION. Plutonium ions tend to form complex ions in the following order:

$$Pu^{+4} > Pu^{+3} \approx PuO_2^{+2} > PuO_2^{+1}$$

Divalent anions tend to form stronger complexes, and the order for simple anions with Pu^{+4} is:

carbonate > oxalate > sulfate > fluoride > nitrate >
chloride > bromide > iodide > perchlorate

Complexation is preferably through oxygen and fluorine rather than nitrogen, phosphorus, or sulfur. Plutonium also forms complexes with ligands such as phosphate, acetate, and tributylphosphate (TBP). Strong chelate complexes form with EDTA, tartrate, citrate, 2-thenoyltrifluoroacetone (TTA), acetylacetone (acac), and cupferron. Plutonium(IV) forms a strong complex with fluoride (PuF^{+3}) that is used to solubilize plutonium oxides and keep it in the aqueous phase during extraction of other elements with organic solvents. The complex with nitrate, $Pu(NO_3)_6^{-2}$, allows the recovery of plutonium from nuclear fuels. Carbonate and acetate complexes prevent precipitation of plutonium from solution even at relatively high pH.

Dissolution of Samples

Metallic plutonium dissolves in halogen acids such as hydrochloric acid, but not in nitric or concentrated sulfuric acids. The metal dissolves in hydrofluoric nitric acid mixtures. Plutonium oxide dissolves with great difficulty in usual acids when ignited. Boiling with concentrated nitric acid containing low concentrations of hydrofluoric acid or with concentrated phosphoric acid is used. Fusion methods have also been used to dissolve the oxide as well as other compounds of plutonium. Plutonium in biological samples is readily soluble, in the case of metabolized plutonium in excreted samples, or highly refractory, in the case of fallout samples. Most procedures for fallout or environmental samples involve treatment with hydrofluoric acid or fusion treatment with a base.

Separation Methods

Extensive work has been done on methods to separate plutonium from other elements. Both laboratory and industrial procedures has received considerable treatment. The methods described below represents only a brief approach to separation of plutonium, but they indicate the nature of the chemistry employed.

PRECIPITATION AND COPRECIPITATION. Macro quantities of plutonium are readily precipitated from aqueous solution, and the methods is the basis of separating plutonium from other radionuclides in some procedures. Contamination of other metals can be a problem, however; zirconium and ruthenium give the most trouble. Plutonium is precipitated primarily as the hydroxide, fluoride, peroxide, or oxalate. Both Pu(III) and Pu(IV) are precipitated from acid solution by potassium or ammonium hydroxide as hydrated hydroxides or hydrous oxides. On redissolving in acid, Pu (IV) tends to form the polymer, and high concentration of acid is needed to prevent its formation. Pu(IV) peroxide is formed on the addition of hydrogen peroxide to Pu(III), Pu(IV), Pu(V), and Pu(VI) because of the oxidizing nature of hydrogen peroxide. The procedure has been used to prepare highly pure plutonium compounds from americium and uranium.

Coprecipitation of plutonium can be very specific with the control of its oxidation states and selection of coprecipitating reagents. Lanthanum fluoride, a classical procedure for coprecipitation of plutonium, will bring down Pu(III) and Pu(IV) but not Pu(VI). Only elements with similar redox and coprecipitation behavior interfere. Separation from other elements as well as concentration from large volumes with lanthanum fluoride is also important because not many elements form acid-soluble lanthanum fluoride coprecipitates. Bismuth phosphate ($BiPO_4$) is also used to coprecipitate Pu(III) and Pu(IV). In contrast to lanthanum fluoride and bismuth phosphate, zirconium phosphate ($ZrPO_4$) and an organic coprecipitate, zirconium phenylarsenate [$Zr(C_6H_5)AsO_4$], will coprecipitate Pu(IV) exclusively.

SOLVENT EXTRACTION. A wide variety of organic extractants have been developed to separate plutonium from other radionuclides and metals by selectively extracting them from aqueous media. The extractants, among others, include organophosphorus compounds such as phosphates (organoesters of phosphoric acid), amines and their quaternary salts, alcohols, ketones, ethers, and amides. Chelating agents such as thenoyltrifluoroacetone (TTA) and cupferron have also been used. Numerous studies have been performed on the behavior of these systems. It has been found that the performance of an extracting system is primarily related to the organic solvent in which the extractant is dissolved and the concentration of the extractant in the solvent, the nature of the aqueous medium (the acid present and its concentration (pH) and the presence of salting

agents), the temperature of the system, and the presence and nature of oxidizing agents. One common system, used extensively in the laboratory and in industrial process to extract plutonium from fission products, illustrates the use of solvent extraction to separate plutonium from uranium and other metals. The PUREX process (plutonium uranium reduction extraction) is used in most fuel reprocessing plants to separate the radionuclides. It employs TBP, tri-*n*-butyl phosphate [$(C_4H_9)_3PO$], in a hydrocarbon solvent, as the extractant. The uranium fuel is dissolved in nitric acid as Pu(III), and plutonium is oxidized to Pu(IV) and uranium to U(VI) by oxidizing agents. Plutonium and uranium are extracted into a 30 percent TBP solution, and the organic phase is scrubbed with nitric acid solution to remove impurities. The plutonium is removed by back-extracting it as Pu(III) with a nitric acid solution containing a reducing agent.

Solvent extraction chromatography has provided an efficient, easy technique for rapidly separating plutonium and other transuranic elements. A process using octylphenyl-N,N-diisobutyl carbamoylphoshpine oxide (CMPO) in TBP and fixed on an inert polymeric resin matrix has been used to isolate plutonium (IV). All plutonium in the analyte is adjusted to plutonium (IV), and the column is loaded from 2 M nitric acid. Plutonium is eluted with 4 M hydrochloric acid and 0.1 M hydroquinone or 0.1 M ammonium hydrogen oxalate ($NH_4HC_2O_4$). It is important to note that iron, found in most environmental samples, does not effect the separation if the element is kept in the +2 oxidation state as ferrous ions. This is commonly achieved using ascorbic acid. The ferric ion (Fe^{+3}) is detrimental to the separation.

ION-EXCHANGE CHROMATOGRAPHY. Ion-exchange chromatography has been used extensively for the radiochemical separation of plutonium. All cationic plutonium species in non-complexing acid solutions readily exchanges onto cation resins at low acid concentrations and desorb at high acid concentrations. Plutonium in all its oxidation states form neutral or anionic complexes with various anions, providing an alternate means for eluting the element. Various cation-exchange resins have been used with hydrochloric, nitric, perchloric, and sulfuric acids for separation of plutonium from metals including other actinides, but the most common use of plutonium cation-exchange chromatography is concentrating a dilute solution or separation from nonabsorbable impurities such as organic reagents, redox agents, for example.

Anion-exchange chromatography is the primary ion-exchange method for the separation of plutonium from other metals and the separation of the plutonium oxidation states, and many procedures have been developed using this method. On a strong anion-exchange resin, for example, the higher oxidation states (IV, V, and VI) occurs at hydrochloric acid concentrations above 6 M, while desorption occurs at 2 M acid. Plutonium (III) does not absorb on the column, and plutonium (VI) absorbs from 2 to 3 M hydrochloric acid solution. Plutonium can be separated from other actinides and most other elements by absorbing the plutonium cations—

Pu(IV) and Pu (VI)—onto a strong-anion resin from 6 M hydrochloric acid, and subsequently eluting the plutonium by reducing it to plutonium III. Anion exchange in 7 to 8 M nitric acid is also an effective method for separating plutonium. The radionuclide loads on the column as $Pu(NO_3)_6^{-2}$ and is eluted with dilute acid or after reduction.

ELECTRODEPOSTION. Separation methods based on elecrtodeposition are not common, but one method for the alpha analysis of plutonium is in use. Plutonium is electrodeposited on a stainless steel disc from an ammonium sulfate solution at 1.2 amps for one hour. The separation is used after isolating the radionuclide by extraction chromatography, and the plutonium isotopes are resolved by alpha spectroscopy.

Methods of Analysis

^{238}Pu, ^{239}Pu, ^{240}Pu, and ^{241}Pu are collected for analysis either by electrodepositon on a platinum or nickel disc or by microprecipitation with lanthanum fluoride (LaF_3). Radionuclides of ^{238}Pu, ^{239}Pu, and ^{240}Pu are determined by alpha spectrometry or gas flow proportional counting. ^{241}Pu is beta counted. ^{236}Pu or ^{242}Pu are used as a tracer for measuring chemical yield. They are measured by alpha spectrometry.

Compiled from: Baes and Mesmer, 1976; Choppin et al., 1995; Coleman, 1965; Cotton and Wilkinson, 1988; DOE 1990, 1995, and 1997; EPA 1973 and 1980; Metz and Waterbury, 1962; Seaborg and Loveland, 1990; Weigel et al., 1986.

14.10.9.6 Radium

Radium, with an atomic number of 88, is the heaviest (last) member of the family of alkaline earth metals, which, in addition, includes beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr), and barium (Ba). It is the most basic and reactive of the series, and exists exclusively as +2 cations in compounds and solution. All isotopes are radioactive, and essentially all analyses are made by radioactive measurements.

Isotopes

There are 25 isotopes of radium from ^{205}Ra to ^{234}Ra; all are radioactive. The most important with respect to the environmental contamination are members of the ^{238}U and ^{232}Th naturally occurring decay series: ^{226}Ra and ^{228}Ra, respectively. ^{226}Ra is the most abundant isotopic form with a half-life of 1,602 years. As a member of the ^{238}U series, it is produced by alpha emission from ^{230}Th. ^{226}Ra emits an alpha particle and, in turn, produces ^{222}Rn, an inert gas that is also an alpha

4400 emitter. Radium generates radon at the rate of 0.1 μL per day per gram of radium, and its
4401 radioactivity decreases at the rate of about one percent each 25 years. ^{228}Ra, half-life of 5.77
4402 years, is produced in the ^{232}Th decay series by emission of an alpha particle from ^{232}Th itself.

4403 Occurrence

4404 In nature, radium is primarily associated with uranium and thorium, particularly in the uranium
4405 ores—carnotite and pitchblende, where ^{226}Ra is in radioactive equilibrium with ^{238}U and its other
4406 progeny. The widespread dispersal of uranium in rocks and minerals results in a considerable
4407 distribution of radium isotopes throughout nature. It is generally found in trace amounts in most
4408 materials, therefore, the radium/uranium ratio is about 1 mg radium per 3 kg uranium (1 part in 3
4409 x 10^6 parts uranium). This leads to a terrestrial abundance of approximately 10^{-6} ppm: 10^{-12}g/g in
4410 rocks and minerals. Building materials, such as bricks and concrete blocks for example, that
4411 contain mineral products also contain radium. With leaching from soil, the concentration is about
4412 10^{-13}g/L in river and streams, and uptake in biological systems produces concentrations of
4413 10^{-14}g/g in plants and 10^{-15}g/g in animals.

4414 Uranium ores have been processed with hot mineral acids or boiling alkali carbonate to remove
4415 radium and/or uranium. Extracted radium was usually coprecipitated with barium sulfate,
4416 converted to carbonate or sulfide, and solubilized with hydrochloric acid. Separation from
4417 barium was usually accomplished by fractional crystallization of the chlorides, bromides, or
4418 hydroxides, since barium salts are usually slightly more soluble. The free metal has been
4419 prepared by electrolysis of radium chloride solutions, using a mercury cathode. The resulting
4420 amalgam is thermally decomposed in a hydrogen atmosphere to produce the pure metal. The
4421 waste streams from these industrial operations contain radium, primarily as a coprecipitate of
4422 barium sulfate. Since many other natural ores also contain uranium and radium, processing can
4423 result in uranium and its equilibrium progeny appearing in a product or byproduct. Apatite, a
4424 phosphate ore, is used to produce phosphoric acid, and the gypsum byproduct contains all the
4425 radium originally present in the ore.

4426 ^{226}Ra extracted from ores has historically been used in diverse ways as a source of radioactivity.
4427 It has been mixed with a scintillator to produce luminous paint, and at one time, the most
4428 common use for its salts was radiation therapy. As a source of gamma radiation, radium activity
4429 was enhanced by sealing a radium salt in a capsule that prevented escape of the gaseous progeny,
4430 ^{222}Rn, and allowing the radon to decay into its successive progeny. Two progeny are ^{214}Pb and
4431 ^{214}Bi, the principal emitters of gamma radiation in the source. For the most part radium has been
4432 replaced in medical technology by other sources of radioactivity, but numerous capsules
4433 containing the dry, concentrated substances still exist.

Radium salts are used in various instruments for inspecting structures such as metal castings by gamma-ray radiography, to measure the thickness of catalyst beds in petroleum cracking units, and to continuously measure and control the thickness of metals in rolling mills. Radium is also used for the preparation of standard sources of radiation, as a source of actinium and protactinium, and as a source of ionizing radiation in static charge eliminators. In combination with beryllium, it is a neutron source for research, in the analysis of materials by neutron activation, and radio-logging of oil wells.

Radium in the environment is the result of natural equilibration and anthropogical activity such as mining and processing operations. Radium is retained by many rock and soil minerals, particularly clay minerals, and migrates only very slowly in through these materials. The decay progeny of ^{226}Ra, gaseous ^{222}Rn, is an important environmental pollutant and represents the most significant hazard from naturally occurring radium. Concentration of the alpha-emitting gas in some occupied structures contributes to the incidence of lung cancer in humans. During the decay of ^{226}Ra, the recoil of the parent nucleus after it emits an alpha particle, now ^{222}Rn, causes an increased fraction of radon to escape from its host mineral, a larger fraction than can be explained by intramineral migration or diffusion.

In groundwater, radium likely encounters dissolved sulfate and/or carbonate anions, which could precipitate radium sulfate or radium carbonate. Although both salts are relatively insoluble, a sulfate concentration of 0.0001 M would still allow an equilibrium concentration of about 0.1 ppm Ra^{+2} to exist in solution. Thus, the insolubilities of either of these salts are not likely to prevent contamination of the environment.

Radium also contaminates the environment because of past disposal practices of some processing, milling, and reclamation operations. Radium process tailings have been discovered in land areas as seams or pockets of insoluble radium compounds, such as barium radium sulfate, or unprocessed radium (uranium) ore, such as carnotite. Release of solid or liquid process streams and subsequent mixing with local soil has resulted in intimate contamination of soil particles, primarily as Ra^{+2} absorbed onto clay-sized fractions. This form of absorbed radium is tightly bound to soil but can be extracted partially by hot concentrated acid solutions.

Solubility of Compounds

The solubility of radium compounds can usually be inferred from the solubility of the corresponding barium compound and the trend in the solubilities of the corresponding alkaline earth compounds. The common water-soluble radium salts are the chloride, bromide, nitrate, and hydroxide. The fluoride, carbonate, phosphate, biphosphate (hydrogen phosphate), and oxalate

are only slightly soluble. Radium sulfate is the least soluble radium compound known, insoluble in water and dilute acids, but it is soluble in concentrated sulfuric acid, forming a complex ion with sulfate anions, $Ra(SO_4)_2^{-2}$.

Radium compounds are essentially insoluble in organic solvents. In most separation procedures based on extraction, other elements, not radium, are extracted into the organic phase. Exceptions are known (see "Separation," below), and crown ethers have been developed recently that selectively remove radium from an aqueous environment.

Review of Properties

Radium is highly toxic exclusively because of its radioactive emissions: gamma radiation of the element itself and beta particles emitted by some of its decay progeny. It concentrates in bones replacing calcium and causing anemia and cancerous growths. Its immediate progeny, gaseous radon, is an alpha emitter that is a health threat when inhaled.

Metallic radium is brilliant white and reacts rapidly with air, forming a white oxide and black nitride. It is an active metal that reacts with cold water to produce radium hydroxide, hydrogen, and other products. The radium ion in solution is colorless. Its compounds also are colorless when freshly prepared but darken and decompose on standing because of the intense alpha radiation. The original color returns when the compound is recrystallized. Alpha emissions also cause all radium compounds to emit a blue glow in air when sufficient quantities are available. Radium compounds also are about 1.5 °C higher in temperature than their surroundings because of the heat released when alpha particles loose energy on absorbance by the compound. Glass containers turn purple or brown in contact with radium compounds and eventually the glass crystallizes and becomes crazed.

Like all alkaline earths, radium contains two valence electrons ($7s^2$) and forms only +2 ions in its compounds and in solution. The ionic radius of radium in crystalline materials is 152 pm (0.152 nm or 1.52 Å), the largest crystalline radius of the alkaline earth cations ($Ra^{+2} > Ba^{+2} > Sr^{+2} > Ca^{+2} > Mg^{+2} > Be^{+2}$). In contrast, the hydrated ion radius in solution is the smallest of the alkaline earth cations, 398 pm ($Be^{+2} > Mg^{+2} > Ca^{+2} > Sr^{+2} > Ba^{+2} > Ra^{+2}$). With the smallest charge-to-crystal-radius ratio among the alkaline earths of 1.32 (+2/1.52), the smallest hydrated radius of radium is expected, because the ratio represents the least attractive potential for water molecules in solution.

4497 Solution Chemistry

4498 Existing exclusively in one oxidation state (+2), the chemistry of radium is uncomplicated by
4499 oxidation-reduction reactions that could produce alternate states in solution. It is made even less
4500 complicated by its weak tendency to form complex ions or hydrolyze in solution. These
4501 properties are a reflection of the small charge-to-crystal-radius ratio of 1.32, described above. In
4502 general, radiochemical equilibrium is established with carriers by stirring, followed by either
4503 standing or digesting in the cold for several minutes. Adsorption of trace amounts of radium on
4504 surfaces, however, is an important consideration in its radiochemistry.

4505 COMPLEXATION. Radium, like other alkaline-earth cations, forms few complexes in acid
4506 solution. Under alkaline conditions, however, several one-to-one chelates are formed with
4507 organic ligands: among others, with EDTA, diethylenetriaminepentaacetate (DTPA),
4508 ethyleneglycol bis(2-aminoethylether)-tetraacetate (EGTA), nitrilotriacetate (NTA or NTTA),
4509 and citrate. The most stable complex ion forms with DTPA. The tendency to form complexes
4510 decreases as their crystalline size increases and their charge-crystal-radius ratio decreases. Since
4511 crystalline sizes of the cations are in the order: $Ra^{+2} > Ba^{+2} > Sr^{+2} > Ca^{+2}$, radium has the least
4512 tendency to form complex ions, and few significant complexes of radium with inorganic anions
4513 are known. One notable exception is observed in concentrated sulfuric acid, which dissolves
4514 highly insoluble radium sulfate ($RaSO_4$) by forming $Ra(SO_4)_2^{-2}$.

4515 Complex-ion chemistry is not used in most radium radiochemical procedures. Complexing
4516 agents are primarily employed as elution agents in cation exchange, in separations from barium
4517 ions by fractional precipitation, and in titration procedures. Alkaline citrate solutions have been
4518 used to prevent precipitation of radium in the presence of lead and barium carriers until complete
4519 isotopic exchange has been accomplished.

4520 HYDROLYSIS. Similar to their behavior complex-ion formation, alkaline earths show less and less
4521 tendency to hydrolyze with increasing size of the ions, and the tendency decreases with
4522 increasing ionic strength of the solution. Therefore, hydrolysis of radium is an insignificant factor
4523 in their solution chemistry.

4524 ADSORPTION. The adsorption of trace amounts of radium on surfaces is an important considera-
4525 tion in its radiochemistry. Although not as significant with radium as with some ions with higher
4526 charges, serious losses from solution can occur under certain conditions. Adsorption on glass is a
4527 particular problem, and adsorption on polyethylene has been reported. Adsorption gradually
4528 increases with increasing pH and depends strongly on the nature of the surface. In the extreme,
4529 up to 50 percent radium has been observed to adsorb onto glass from neutral solution in 20 days,

and 30 percent from 0.13 M hydrochloric acid (HCl). Fortunately, adsorbed radium can be removed from glass with strong acid.

The presence of insoluble impurities, such as traces of dust or silica, increases adsorption, but adsorption is negligible from very pure solutions at low pH values. Tracer radium solutions, therefore, should be free from insoluble impurities, and radium should be completely in solution before analysis. The solutions should also be maintained in at least 1 M mineral acid or contain chelating agents. Addition of barium ion as a carrier for radium will probably decrease the amount of radium adsorption. Radium residues from solubilization of samples that contain silica or lead or barium sulfates and those that result in two or more separate solutions should be avoided since the radium might divide unequally between the fractions. Destruction of silica with HF, reduction of sulfates to sulfides with zinc dust, and subsequent dissolution of the residue with nitric acid are procedures used to avoid this problem.

Dissolution of Samples

Soil, mineral, ore samples, and other inorganic solids are dissolved by conventional treatment with mineral acids and by fusion with sodium carbonate (Na_2CO_3). Hydrofluoric acid (HF) or potassium fluoride (KF) is used to remove silica. Up to 95 percent radium removal has been leached from some samples with hot nitric acid (HNO_3), but such simple treatment will not completely dissolve all the radium in soil, rock, and mineral samples. Biological samples are wet ashed first with mineral acids or decomposed by heating to remove organic material. The residue is taken up in mineral acids or treated to remove silica. Any dissolution method that results in two or more separate fractions should be avoided, since the adsorption characteristics of trace quantities of radium may cause it to divide between the fractions.

Barium sulfate ($BaSO_4$), often used to coprecipitate radium from solution, can be dissolved directly into alkaline EDTA solutions. Radium can be repeatedly reprecipitated and dissolved by alternate acidification with acetic acid and dissolution with the EDTA solution.

Solutions resulting from dissolution of solid samples should be made at least 1 M with mineral acid before storage to prevent radium from absorbing onto the surface of glass containers.

Separation Methods

COPRECIPITATION. Radium is almost always present in solution in trace amounts, and even the most insoluble radium compound, radium sulfate, can not be used to separate and isolate radium from solution by direct precipitation. Therefore, the cation is commonly removed from solution

in virtually quantitative amounts by coprecipitation. Since radium forms the same types of insoluble compounds as barium: sulfates (SO_4^{-2}), chromates (CrO_4^{-2}), carbonates (CO_3^{-2}), phosphates (PO_4^{-3}), oxalates ($C_2O_4^{-2}$), and sulfites (SO_4^{-2}), it coprecipitates with all insoluble barium compounds, and to a lesser extent with most insoluble strontium and lead compounds. Barium sulfate and barium chromate are most frequently used to carry radium during coprecipitation. Other compounds that are good carriers for radium include: ferric hydroxide when precipitated at moderately high pH with sodium hydroxide (NaOH) or ammonium hydroxide (NH_4OH), barium chloride ($BaCl_2$) when precipitated from a cold mixed solvent of water and alcohol saturated with hydrochloric acid, barium iodate ($BaIO_3$), and various insoluble phosphates, fluorides (F^{-1}), and oxalates (e.g., thorium phosphate [$Th_3(PO_4)$], lanthanum fluoride (LaF_3), and thorium oxalate [$Th(C_2O_4)$]. Lead sulfate ($PbSO_4$) can be used if a carrier-free radium preparation is required, since quantitative lead-radium separations are possible while quantitative barium-radium separations are very difficult.

ION EXCHANGE. Radium has been separated from other metals on both cation- and anion-exchange resins. Barium and other alkaline earths are separated on cation-exchange columns under acidic conditions. In dilute hydrochloric acid solutions (3 M), the affinity of the cation for the exchange site is dominated by ion-dipole interactions between the water molecules of the hydrated ion and the resin. Ions of smaller hydrated radius (smaller charge-to-crystal-radius ratio) tend to displace ions of larger hydrated radius. The affinity series is $Ra^{+2}>Ba^{+2}>Sr^{+2}>Ca^{+2}$, and radium elutes last. Increasing the acid concentration to 12 M effectively reverses the order of affinity, since the strong acid tends to dehydrate the ion, and ion-resin affinity is dominated more by ionic interactions, increasing in the order of increasing crystal radius: $Ca^{+2}>Sr^{+2}>Ba^{+2}>Ra^{+2}$, and calcium elutes last. Radium has also been separated from tri- and tetravalent ions since these ions have a much stronger affinity for the cation-exchange resin. Radium with its +2 charge is only partially absorbed, while trivalent actinium and tetravalent thorium, for example, will be completely absorbed. Tracer quantities of radium also has been separated from alkaline earths by eluting a cation-exchange column with chelating agents such as lactate, citrate, and EDTA; radium typically elutes last, since it forms weaker interactions with the ligands.

Anion-exchange resins have been used to separate radium from other metal ions in solutions of chelating agents that form anionic complexes with the cations. The affinity for the columns decreases in the order Ca > Sr > Ba > Ra, reflecting the ability of the metal ions to form stable complex anions with the chelating agents. The difficult separation of barium from radium has been accomplished by this procedure. Radium is also separated from metals such as uranium, polonium, bismuth, lead, and protactinium that form polychloro complex anions. Since radium does not form a chlorocomplex, it does not absorbs on the anion exchanger (carrying a positive charge), and remains quantitatively in the effluent solution.

Ion-exchange methods are not easily adapted for the separation of macro-scale quantities of radium, because the intense radiation degrades the synthetic resin and insoluble radium compounds usually form in the ion-exchange column.

SOLVENT EXTRACTION. Radium compounds have very low solubilities in organic solvents. In most extraction procedures, other organic-soluble complexes of elements, not radium, are extracted into the non-aqueous phase, leaving radium in the water. Radium is separated from actinium, thorium, polonium, lead, bismuth, and thallium, for example, by extracting these elements as 2-thenoyltrifluoroacetone (TTA) complexes. Radium does not form the complex except at very high pH, and is not extracted. One notable exception to this generality is the extraction of radium tetraphenylborate by nitrobenzene from an alkaline solution. The presence of EDTA inhibits formation of the tetraphenylborate, however, and radium is not extracted in the presence of EDTA either.

More recent developments have employed crown ethers to selectively extract radium as a complex ion from water samples for analysis. Radium-selective extraction membranes have also been used to isolate radium from solutions.

Methods of Analysis

Radium is detected and quantified by counting either alpha or gamma emissions of the radionuclide or its progeny. Gamma-ray spectroscopy can be used on macro ^{226}Ra samples (approximately 50 g or more) without pretreatment unless ^{235}U, even in very small quantities, is present to interfere with the measured peak. The most sensitive method for the analysis of ^{226}Ra is de-emanation of ^{222}Rn from the radium source, complete removal, followed by alpha counting the ^{222}Rn and its progeny. The procedure is lengthy and expensive, however. The radium in a liquid sample is placed in a sealed tube for a specified time to allow the ingrowth of ^{222}Rn. The radon is collected in a scintillation cell and stored for several hours to allow for ingrowth of successive progeny products. The alpha radiation is then counted in the scintillation cell called a Lucas cell. The primary alpha emissions are from ^{222}Rn, ^{218}Po, and ^{214}Po. Complete retention of radon can also be accomplished by sealing the radium sample hermetically in a container and alpha- or gamma-counting.

^{228}Ra can also be determined directly by gamma spectroscopy, using the gamma-rays of its progeny, ^{228}Ac, without concern for interference; however, a lower detection limit is obtained if the ^{228}Ac is measured by beta counting. In the beta-counting procedure, ^{228}Ra is separated, time is allowed for actinium ingrowth, the ^{228}Ac is removed by solvent extraction, ion-exchange, or coprecipitation, and then measured by beta counting.

^{224}Ra can be determined by chemically isolating the ^{212}Pb, which is in equilibrium with the ^{224}Ra. After an appropriate ingrowth period, ^{212}Pb is determined by alpha counting its progeny, ^{212}Bi and ^{212}Po.

Compiled from: Baes and Mesmer, 1976; Choppin et al., 1995; Considine and Considine, 1983; DOE, 1990 and 1997, 1997; EPA, 1984; Friedlander et al., 1981; Green and Earnshaw, 1984; Hassinsky and Asloff, 1965; Kirby and Salutsky, 1964; Lindsay, 1988; Salutsky, 1997; Sedlet, 1966; Shoesmith, 1964; Sunderman and Townley, 1960; Turekian and Bolter, 1966; Vdovenko and Dubasov, 1975.

14.10.9.7 Strontium

Strontium, atomic number 38, is the fourth member of the alkaline-earth metals, which includes beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba), and radium (Ra). Like radium, it exist exclusively in the +2 oxidation state in both compounds and in solution, making its chemistry simpler than many of the radionuclides reviewed in this section.

Isotopes

Strontium exists in 29 isotopic forms, including three metastable states, ranging in mass number from 77 to 102. Natural strontium is a mixture of four stable isotopes: ^{84}Sr, ^{86}Sr, ^{87}Sr, and ^{88}Sr. The lower mass number isotopes decay by electron capture, and the isotopes with higher mass numbers are primarily beta emitters. The half-lives of most isotopes are short, measured in milliseconds, seconds, minutes, hours, or days. The exception is ^{90}Sr, a beta emitter with a half-life of 29.1 years.

Occurrence and Uses

Strontium is found in nature in two main ores, celestite ($SrSO_4$) and strontianite ($SrCO_3$), widely distributed in small concentrations. Small amounts are found associated with calcium and barium minerals. The earth's crust contains 0.042 percent strontium, ranking twenty-first among the elements occurring in rock and making it as abundant as chlorine and sulfur. The element ranks 11th in abundance in sea water, about 8-10 ppm. The only naturally occurring radioactive isotopes of strontium are the result of spontaneous fission of uranium in rocks. Other nuclear reactions and fallout from nuclear weapons test are additional sources of fission products. ^{90}Sr is a fission product of ^{235}U, along with ^{89}Sr, and short-lived isotopes, ^{91}Sr to ^{102}Sr. ^{85}Sr can be produced by irradiation of ^{85}Rb with accelerated protons or deuterons.

Separation Techniques

Stable strontium is produced from its ores. The sulfate ore is leached with hydrochloric acid solution to remove impurities and shaken with sodium carbonate for several hours to produce strontium carbonate. Washing this product or the carbonate ore with hot water and several reprecipitation steps produce a fine grade of strontium carbonate. The metal is produced by converting the carbonate to strontium chloride with hydrochloric acid or to strontium oxide by heating. Strontium chloride in a melt with potassium chloride is electrolyzed or the oxide is reduced by heating with aluminum in a vacuum to distill off the metal. An alternate method electrolyzes an aqueous solution of the chloride with a mercury cathode. The resultant mercury amalgam is heated in hydrogen to drive off the mercury.

The major use of strontium is in glass production for color television picture tubes. Strontium is used in producing ferrite magnets, in refining zinc, to produce hardness and durability in alloys of tin and lead, as a deoxidizer in copper and bronze, and "getter" in electron tubes. Strontium hydroxide forms soaps and greases with numerous organic acids that are stable, resistant to oxidation and decomposition over a wide temperature range, and resistant to decomposition by water and the leaching action of hydrocarbons. The beta emission of ^{90}Sr and its progeny, ^{90}Y ($t_{1/2}$=64 h), has found applications in industry, medicine, and research. The radionuclides are in equilibrium in about 25 days. The radiation of ^{90}Y is more penetrating than that of strontium. It is used with zinc sulfide in some luminescent paints. Implants of ^{90}Sr provide radiation therapy for the treatment of the pituitary gland and breast and nerve tissue. The radiation from strontium has been used in thickness gauges, level measurements, automatic control processes, diffusion studies of seawater, and a source of electrical power. Since ^{90}Sr is one of the long-lived and most energetic beta emitters, it might prove to be a good source of power in space vehicles, remote weather stations, navigational buoys, and similar long-life, remote devices. Both ^{89}Sr and ^{90}Sr have been used in physical chemistry experiments and in biology as tags and tracers. ^{90}Sr to ^{87}Sr ratios are used in geological dating, because ^{87}Sr is formed by decay of long-lived ^{87}Rb.

Solubility of Compounds

Several simple salts of strontium are soluble in water. Among these are the acetate, chloride, bromide, iodide, nitrate, nitrite, permanganate, sulfide, chlorate, bromate, and perchlorate. Strontium hydroxide is slightly soluble and is precipitated only from concentrated solutions.

Review of Properties

Strontium is a low-density (2.54 g/cm^3) silver-white metal. It is as soft as lead and is malleable and ductile. Three allotropic forms exit with transition temperatures of 235 and 540 °C. Freshly

cut strontium is silver in appearance, but it rapidly turns a yellowish color on formation of the oxide in the air. It is stored under mineral oil to prevent oxidation.

The metal decomposes water, producing strontium hydroxide [$Sr(OH)_2$] and hydrogen, and the finely divided metal ignites spontaneously in the air. The hydroxide forms strontium peroxide (SrO_2) when treated with hydrogen peroxide in the cold. Strontium is a strong reducing agent and combines directly with hydrogen, halogens, oxygen, and sulfur to form, respectively, the simple binary compounds: hydride (SrH_2), halogens (SrX_2), oxide (SrO), and sulfide (SrS). The metal reacts with nitrogen to form the nitride (Sr_3N_2) only on heating to 380 °C. It also reacts vigorously with most acids to form Sr^{+2} salts and hydrogen. With nitric acid the reaction is fast, producing nitrogen dioxide. In contrast, reaction with sulfuric acid is slow because of the formation of the insoluble sulfate [$Sr(SO_4)_2$].

Strontium isotopes are some of the principal constituents of radioactive fallout following detonation of nuclear weapons, and they are released in insignificant amounts during normal operations of reactors and fuel reprocessing operations. Their toxicity is higher, however, than that of other fission products, and ^{90}Sr represent a particular hazard because of its long half-life, energetic beta emission, tendency to contaminate food, especially milk, and high retention in bone structure. Strontium in bone is difficult to eliminate and has a biological half-life of approximately eleven years (4,000 d).

Strontium occurring in groundwater is primarily in the form of strontium carbonate. Its solubility under oxidizing and reducing conditions is approximately 0.001 M (0.15 g/L or 150 g/m^3).

Solution Chemistry

Strontium exists exclusively in the +2 oxidation state in solution, so the chemistry of strontium is uncomplicated by oxidation-reduction reactions that could produce alternate states in solution.

COMPLEXATION. Strontium has little tendency to form complexes. Of the few complexing agents for strontium, the significant agents in radiochemistry to date are EDTA, oxalate, citrate, ammoniatriacetate, methylanine-N,N-diacetate, 8-quinolinol, and an insoluble chelate with picrolonate. The most stable complex ion forms with EDTA. Coordination compounds of strontium are not common. These chelating agents are used primarily in ion-exchange procedures. Amine chelates of strontium are unstable, and the β-diketones and alcohol chelates are poorly characterized. In contrast, cyclic crown ethers and cryptates form stronger chelates with strontium than with calcium, the stronger chelating metal with EDTA and more traditional chelating agents. Cryptates are a macrocyclic chelate of the type, $N[(CH_2CH_2O)_2CH_2CH_2]_3N$, an

octadentate ligand containing six oxygen atoms and two nitrogen atoms as ligand bonding sites that encapsulates the cation. It might find use in the extraction chemistry of strontium.

HYDROLYSIS. The tendency of the alkaline-earth cations to hydrolyze decreases as their atomic number increases. The tendency is greater than that of the corresponding alkali metals, but hydrolysis of potassium, for example, is insignificant. An indication of the tendency of a cation to hydrolyze is the solubility of their hydroxides, and the solubility of the alkaline earths become more soluble with increasing atomic number. Strontium hydroxide is slightly soluble in water (8 g/L at 20 °C). In comparison, the hydroxide of beryllium, the first element in the alkaline earth series, has a solubility of approximately 3×10^{-4} g/L.

Dissolution of Samples

Dissolution of samples for the analysis of strontium is generally simple. Water is used to dissolve soluble compounds: acetate, bromide, chloride, iodide, chlorate, perchlorate, nitrate, nitrite, and permangenate. Hydrochloric or nitric acid dissolves the fluoride, carbonate, oxalate, chromate, phosphate, sulfate, and oxide. Strontium in limestone, cement, soil, bone, and other biological material can be dissolved from some samples in hot hydrochloric acid. Insoluble silica, if present, can be filtered or centrifuged. In some cases, soil can be leached to remove strontium. As much as 99.5 percent of the strontium in some crushed soil samples has been leached with 1 M nitric acid by three extractions. Soil samples have also been suspended overnight in ammonium acetate at pH 7. If leaching is not successful, soil samples can be dissolved by alkali fusion of the ground powder with potassium hydroxide, nitrate, or carbonate. Strontium is taken up from the residue in nitric acid. Biological materials such as plant material or dairy products are solubilized by ashing at 600 °C and taking up milk residue in hot, concentrated hydrochloric acid and plant residue in aqua regia. Wet ashing can be used by treating the sample with nitric acid followed by an equal-volume mixture of nitric and perchloric acids. Human and animal bone samples are ashed at 900 °C and the residue dissolved in concentrated hydrochloric acid.

Separation Methods

PRECIPITATION AND COPRECIPITATION. The common insoluble salts of strontium are the fluoride, carbonate, oxalate, chromate, and sulfate. Most are suitable for radiochemical procedures, and strontium separation have the advantage of stable forms of strontium that can be used as a carrier and are readily available. Precipitation of strontium nitrate in 80 percent nitric acid has been used to separate stable strontium carrier and ^{90}Sr from its progeny, ^{90}Y, and other soluble nitrates (calcium, for example). The solubility of strontium chloride in concentrated hydrochloric solution has been used to separate strontium from barium—barium chloride is insoluble in the

acid. Barium and radium (as coprecipitant) have been removed from strontium by precipitating barium as the chromate at a carefully controlled pH of 5.5. Strontium chromate will not precipitate unless the pH is raised. Strontium can also be separated from yttrium by precipitation of the much less soluble yttrium hydroxide by raising an acid solution of the cations to a pH of about 8 with ammonium hydroxide. Strontium hydroxide is slightly soluble and will not precipitate without high concentrations of hydroxide or strontium or both. Carrier-free strontium is coprecipitated with ferric hydroxide, and lead sulfate is also used.

SOLVENT EXTRACTION. The application of organic solvents for separation of strontium from other metals has not been extensive. Thenoyltrifluoroacetone (TTA) has been used to extract carrier-free strontium at a pH > 10. At pH 5, ^{90}Y is extracted with TTA from strontium, which remains in aqueous solution. 8-hydroxyquinolinol in chloroform has also been used to extract strontium. The few procedures that have been available are mainly used to separate the alkaline earths from each other. A 1:1 mixture of ethyl alcohol and diethy ether extracts calcium from strontium.

In recent years, extraction procedures have been developed based on the complexation of strontium cations with crown ethers in 1-octanol. Strontium can be extracted with these mixture from 1 M to 7 M nitric acid solutions. The most advantageous application of strontium extraction procedures has been found in extraction chromatography. An extraction resin consisting of 4,4'(5')-bis(*t*-butylcyclohexano)-18-crown-6 (DtBuCH18C6) in 1-octanol on an inert polymeric matrix is highly selective for strontium nitrate and will separate the cation from many other metals including calcium, barium, and yttrium. This column is used to separate strontium from potassium, cerium, plutonium, and neptunium (K^{+1}, Ce^{+4}, Pu^{+4}, Np^{+4}, respectively). The column is prepared and loaded from 8 M nitric acid. The ions listed above are eluted with 3 M nitric acid containing oxalic acid. Strontium is eluted with 0.05 M nitric acid.

ION-EXCHANGE CHROMATOGRAPHY. Ion-exchange chromatography is used to separate trace quantities of strontium, but separation of macro quantities is very time consuming. Strontium is absorbed on cation-exchange resins, and elution is often based on the formation of a stable complex. Carrier-free strontium is separated from fission products, including barium, on a cation-exchange resin and eluted with citrate. In a similar process, strontium was also separated form other alkaline earths, magnesium, calcium, barium, and radium, eluting with ammonium lactate at pH 7 and 78 °C. Good separations were also obtained with hydrochloric solutions and ammonium citrate. ^{90}Sr and ^{90}Y are separated on a cation-exchange column, eluting yttrium with ammonium citrate at pH 3.8 and strontium at pH 6.0. Strontium and calcium have also been separated in EDTA solutions at pH 5.3. Strontium is retained on the column, and calcium elutes as the calcium-EDTA complex. Strontium elutes with 3 M hydrochloric acid.

Not many procedures use anion-exchange chromatography for separation of strontium. ^{90}Sr has been separated from ^{90}Y on an anion-exchange resin pretreated with hydroxide. Strontium is eluted form the column with water, and yttrium is eluted with 1 M hydrochloric acid. The alkaline earths have been separated by anion-exchange column pretreated with dilute ammonium citrate, loading the column with the chloride form of the metals, and eluting with ammonium citrate at pH 7.5.

Methods of Analysis

Macroquantities of strontium are determined by gravimetric methods and atomic absorption spectrometry, and emission spectrometry. Strontium is precipitated as strontium carbonate or sulfate in gravimetric procedures. For atomic absorption analysis, the separated sample is ashed, and the product is dissolved in hydrochloric acid. Lanthanum is added to the solution to precipitate interfering anions, phosphate, sulfate, or aluminate, that would occur in the flame.

^{89}Sr and ^{90}Sr are determined by analysis of their beta emissions. With a short half-life of 53 d, ^{89}Sr is only found in fresh fission products. ^{90}Sr is a beta emitter with a half-life of 27.7 y. Its progeny is ^{90}Y, which emits beta particles with a half-life of 64.0 h, producing stable ^{90}Zr. Neither ^{90}Sr nor ^{90}Y is a gamma emitter. ^{90}Sr is determined directly from its beta emission, before ^{90}Y grows in, by beta counting immediately (three to four hours) after it is collected by precipitation. The chemical yield can be determined gravimetrically by the addition of stable strontium, after the separation of calcium. Alternatively, ^{90}Sr can be measured from the beta emission of ^{90}Y while it reaches secular equilibrium (two to three weeks). The ^{90}Y is separated by solvent extraction and evaporated to dryness or by precipitation, then beta counted. The chemical yield of the yttrium procedure can be determined by adding stable yttrium and determining the yttrium gravimetrically. ^{89}Sr has a half-life of 52.7 d and is only present in fresh fission material. If it is present with ^{90}Sr, it can be determined by the difference in activity of combined ^{89}Sr and ^{90}Sr (combined or total strontium) and the activity of ^{90}Sr. Total strontium is measured by beta counting immediately after it is collected by precipitation, and ^{90}Sr is measured by isolating ^{90}Y after ingrowth. ^{85}Sr can be used as a tracer for determining the chemical yield of ^{90}Sr (determined by isolating ^{90}Y), but its beta emission interferes with beta counting of total strontium and must be accounted for in the final activity.

An alternative method for determining ^{89}Sr and ^{90}Sr in the presence of each other is based on the equations for decay of strontium radionuclides and ingrowth of ^{90}Y. Combined strontium is collected and immediately counted to determine the total strontium. During ingrowth, the mixture is recounted, and the data from the counts are used to determine the amount of ^{89}Sr and ^{90}Sr in the original (fresh) mixture.

Compiled from: Baes and Mesmer, 1976; Choppin et al., 1995; Considine and Considine, 1983; CRC, 1998-99; DOE, 1990 and 1997, 1997; EPA, 1973; EPA, 1980; Greenwood and Earnshaw, 1984; Hassinsky and Adloff, 1965; Riley, 1995; Sunderman and Townley, 1960; Turekian and Bolter, 1966.

14.10.9.8 Technetium

Technetium, atomic number 43, was the first element to be made artificially. Techetium has no stable isotopes. Natural technetium is known to exist but only in negligibly small quantities resulting from the spontaneous fission of natural uranium. Technetium is chemically very similar to rhenium, but significant differences exist that cause them to behave quite differently under certain conditions.

Isotopes

Thirty-one radioisotopes and unstable isomers of technetium are known with mass numbers ranging from 86 to 113. The half-lives range from seconds to millions of years. The lower mass number isotopes decay by primarily by electron capture and the higher mass number isotopes by beta emission. The significant isotopes (with half-lives/decay modes) are ^{95m}Tc (61 d/electron capture and isomeric transition), ^{99m}Tc (6.01 h/isomeric transition by low-energy gamma), and ^{99}Tc (2.13×10^5 y/beta to stable ruthenium-99). Other, long-lived isotopes are ^{97}Tc (2.6×10^6/electron-capture) and ^{98}Tc (4.2×10^6 y/beta emission).

Occurrence and Uses

The first synthesis of technetium was through the production of ^{99}Mo by bombardment of ^{98}Mo with neutrons and subsequent beta decay to ^{99}Tc. Technetium is also a major constituent of nuclear reactor fission products and has been found in very small quantities in pitchblende from the spontaneous fission of naturally occurring uranium.

Technetium makes up about 6 percent of uranium fission products in nuclear power plant fuels. It is recovered from these fuels by solvent extraction and ion-exchange after storage of the fuels for several years to allow the highly radioactive, short-lived products to decay. Technetium is recovered as ammonium pertechnate (NH_4TcO_4) after its solutions are acidified with hydrochloric acid, precipitated with sulfide, and the sulfide (Tc_2S_7) is reacted with hydrogen peroxide. Rhenium and molybdenum are also removed by extraction with organic solvents. The metal is obtained by reduction of ammonium pertechnate with hydrogen at 600 °C.

Potassium pertechnates ($KTcO_4$) have been used in water (55 ppm) as corrosion inhibitors for mild carbon steel in aerated distilled water, but currently there is no significant uses of elemental technetium or its compounds, although technetium and some of its alloys are a superconductor. The corrosion protection is limited to closed systems to prevent release of the radioactive isotope. ^{99m}Tc, with a half-life of only 61 days, has been used in tracer work. ^{99m}Tc is used in medical diagnosis as a radioactive tracer. As a complex, the amount of ^{99m}Tc required for gamma scanning is very small, thus, it is referred to as non-invasive scanning. It is used for cardiovascular and brain studies and the diagnosis of liver, spleen, and thyroid disorders. There are more than 20 ^{99m}Tc compounds available commercially for diagnostic purposes. With iodine isotopes, they are the most frequently used radionuclides for diagnostics. ^{99m}Tc has also been used to determine the deadtime of counting detectors.

Solubility of Compounds

The nature of the compounds has not been thoroughly delineated, but ammonium pertechnate is soluble in water, and technetium heptoxide forms soluble pertechnetic acid ($HTcO_4$) when water is added.

Review of Properties

Technetium is a silver-grey metal that resembles platinum in appearance. It tarnishes slowly in moist air to give the oxyacid, pertechnetic acid ($HTcO_4$). It has a density of 11.5 g/cm^3. The metal reacts with oxygen at elevated temperatures to produce the volatile oxide, technetium heptoxide. Technetium dissolves in warm bromine water, nitric acid, aqua regia, and concentrated sulfuric acid, but it is insoluble in hydrochloric and hydrofluoric acids. Technetium forms the chlorides ($TcCl_4$ and $TcCl_6$) and fluorides (TcF_5 and TcF_6) by direct combination of the metal with the respective halogen. The specific halide is obtained by selecting the proper temperature and pressure for its formation.

^{99}Tc has a high specific activity. As a contamination hazard, it should be handled in a glove box.

The behavior of technetium in groundwater is highly dependent on its oxidation state. Under oxidizing conditions, pertechnate is the predominant species. It is very soluble and only slightly absorbed to mineral components. For those reasons, it has a relatively high dissemination potential in natural systems. Under reducing conditions, technetium precipitates as technetium dioxide (TcO_2), which is very insoluble. With the production of ^{99}Tc in fission fuels and considering its long half-life, the soluble form of the radionuclide is an environmental concern wherever the fuel is reprocessed or stored. As a consequence, ^{99}Tc would be expected to be one

of the principle contributors to a radioactive release to the environment, even from repositories with barriers that could retain the radionuclide up to 10,000 years. Studies of a salt repository indicate that ^{99}Tc is one of the few radionuclides that might reach the surface before it decays.

Solution Chemistry

All oxidation states between -1 and +7 can be expected for technetium, but the important ones in solution are +4 and +7. The +4 state exist primarily as the slightly soluble oxide, TcO_2. It is soluble only in the presence of complexing ligands; $TcCl_6^{-2}$, for example, is stable in solutions with a chloride concentration greater than 1 M. The most important species in solution is the pertechnate ion [TcO_4^{-1} as Tc(VII)], which is readily soluble and easily formed from lower oxidation states with oxidizing agents such as nitric acid and hydrogen peroxide. There is no evidence of polymeric forms in solution as a result of hydrolysis of the metal ion.

OXIDATION-REDUCTION BEHAVIOR. Most radioanalytical procedures for technetium are performed on the pertechnate ion, TcO_4^{-1}. The ion can be reduced by hydrochloric acid, the thiocyanate ion (SCN^{-1}), organic impurities, anion-exchange resins, and some organic solvents. The product of reduction can be TcO_2 [Tc(IV)], although a multiplicity of other products are expected in complexing media. Even though the +7 oxidation state is easy to reduce, the reduction process is sometimes slow. Unless precautions are taken to maintain the appropriate oxidation state, however, erratic results will be obtained during the radioanalytical procedure. Several examples illustrate the precaution. Dissolution should always be performed under strongly oxidizing conditions to ensure conversion of all states to the +7 oxidation state since complications because of slow exchange with carrier and other reagents are less likely to occur if this state is maintained. Technetium is extracted with various solvents in several radioanalytical procedures, but the method can be very inefficient because of reduction of the pertechnate ion by some organic solvents. The presence of an oxidizing agent such as hydrogen peroxide will prevent the unwanted reduction. In contrast, TcO_4^{-1} is easily lost on evaporation of acid solutions unless a reducing agent is present or evaporation is conducted at a relatively low temperature.

COMPLEXATION. Technetium forms complex ions in solution with several simple inorganic ligands such as fluoride and chloride. The +4 oxidation state is represented by the TcX_6^{-2} ion where X = F, Cl, Br, and I. It is formed from TcO_4^{-1} by reduction to the +4 state with iodide in HX. TcF_6^{-2} is found in HF solutions during decomposition of samples, before further oxidation.

Complex ions formed between organic ligands and technetium in the +5 oxidation state are known with the general formula, TcO_3XLL, where X is a halide and L is an organic ligand. the

ligands typically bond through an oxygen or nitrogen atom. Other organic complexes of the +5 state have the general formulas: $TcOX_2L_2$, $TcOX_4^{-1}$, and $TcOX_5^{-2}$.

Dissolution of Samples

Dissolution of samples containing technetium requires two precautions: it is essential that acid solutions be heated only under reflux conditions to avoid losses by volatilization, and dissolution should be done only with strongly oxidizing conditions to ensure conversion of all lower oxidation states to Tc(VII). In addition, problems with slow carrier exchange are less likely for the VII oxidation state. Molybdenum targets are dissolved in nitric acid or aqua regia, but the excess acid interferes with many subsequent analytical steps. Dissolution in concentrated sulfuric acid followed by oxidation with hydrogen peroxide after neutralization avoids these problems of excess acid. Other technetium samples can be dissolved by fusion with sodium peroxide/sodium hydroxide (Na_2O_2/NaOH) fluxes.

Separation Methods

PRECIPITATION AND COPRECIPITATION. The various oxidation states of technetium are precipitated in different forms with different reagents. Technetium (VII) is primarily present in solution as the pertechnate anion, and macro quantities are precipitated with large cations such as thallium (Tl^{+1}), silver (Ag^{+1}), cesium (Cs^{+1}), and tetraphenylarsonium [$(C_6H_5)_4As^{+1}$]. the latter ion is the most efficient if ice-bath conditions are used. Perchtechnate is coprecipitated without interference from molybdenum with these cations and perrhenate (ReO_4^{-1}), perchlorate (ClO_4^{-1}), periodate (IO_4^{-1}), and tetrafluoroborate (BF_4^{-1}). The salt consisting of tetraphenylarsenium and the perrhenate froms a coprecipitate fastest, in several seconds. Technetium (VII) can be precipitated from solution as the heptasulfide (Tc_2S_7) by the addition of hydrogen sulfide (or hydrogen sulfide generating compounds such as thioacetamide and sodium thiosulfate) from 4 M sulfuric acid. Since many other transition metals often associated with technetium also from insoluble compounds with sulfide, the method is primarily used to concentrate technetium.

Technetium (IV) is carried by ferric hydroxide. The method can be use to separate technetium from rhenium. The precipitate is solubilized and oxidized with concentrated nitric acid, and iron is removed by precipitation with aqueous ammonia. Technetium is also coprecipitated as the hexachlorotechnate (IV) ($TcCl_6^{-2}$) with thallium and α,α'-dipyridylhexachlororhenate (IV).

Technetium (VI) (probably as TcO_{4-2}) is carried quantitatively by molybdenum 8-hydroxyquinolate and by silver or lead molybdate. Technetium (III) is carried quantitatively by iron or zinc hydroxide and the sulfide, hydroxide, and 8-hydroxyquinolate of molybdenum.

SOLVENT EXTRACTION. Technetium, primarily in the Tc (VII) state (pertechnetate) can be isolated by extraction with organic solvents, but the principal disadvantage of all extraction systems is the inevitable introduction of organic material that might reduce the pertechnetate anion and cause difficulties in subsequent analytical steps. The pertechnetate ion is extracted with pyridine from a 4 M sodium hydroxide solution, but perrhenate and permanganate ions are also extracted. The anion also extracts into chloroform in the presence of the tetraphenylarsonium ion as tetraphenylarsonium pertechnetate. Extraction is more favorable from neutral or basic sulfate solutions than chloride solutions. Perrhenate and perchlorate are also extracted but molybdenum does not interfere. Small amounts of hydrogen peroxide in the extraction mixture to prevent reduction of pertechnetate. Technetium is back-extracted into 0.2 M perchloric acid or 12 M sulfuric acid. Other organic solvents are have also been used to extract pertechnetate from acid solutions, including alcohols, ketones, and tributyl phosphate. Ketones and cyclic amines are more effective for extraction form basic solutions. Tertiary amines and quaternary ammonium salts are more effective extracting agents than alcohols, ketones, and tributyl phosphate. Back extraction is accomplished several ways, depending on the extraction system. A change in pH, displacement by another anion such as perchlorate, nitrate, or bisulfate, or addition of a nonpolar solvent to an extraction system consisting of an oxygen-containing solvent.

A recent extraction method has been used successfully for extraction chromatography and extractive filtration. A column material consisting of trioctyl and tridecyl methyl ammonium chlorides impregnated in an inert apolar polymeric matrix is used to separate ^{99}Tc by loading the radionuclide as the pertechnetate ion from a 0.1 M nitric acid solution. It is stripped off the column with 12 M nitric acid. Alternatively, the extraction material is used in a filter disc, and the samples containing ^{99}Tc are filtered from water at pH 2 and rinsed with 0.01 M nitric acid. Technetium is collected on the disc.

Lower oxidation states of technetium are possible. The thiocyanate complexes of technetium (V) is soluble in alcohols, ethers, ketones, and trioctylphosphine oxide or trioctylamine hydrochloride in cyclohexane or 1,2-dichloroethane. Technetium (IV), as $TcCl_6^{-2}$, extracts into chloroform in the presence of high concentrations of tetraphenylarsonium ion. Pertechnate and perrhenate are both extracted from alkaline solution by hexone (methyl isobutyl ketone), but reduction of technetium to the IV state with hydrazine or hydroxylamine results in the extraction of perrhenate only.

ION-EXCHANGE CHROMATOGRAPHY. Ion-exchange chromatography is primarily performed with technetium as the pertechnate anion. Technetium does not exchange on cation resins, so technetium is rapidly separated from other cations on these columns. In contrast, it is strongly absorbed on strong anion exchangers and is eluted with anions that have a greater affinity for the

resin. Technetium and molybdenum are separated using ammonium thiocyanate as the eluent. A good separation of pertechnate and molybdate has been achieved on an anion-exchange resin in the phosphate form where the molybdate is preferentially absorbed. Good separation of pertechnate and perrhenate are obtained with perchlorate as the eluent.

VOLATILIZATION. The volatility of technetium heptoxide allows the co-distillation of technetium with acids. Co-distillation from perchloric acid gives good yields, but only a partial separation from rhenium is achieved. Molybdenum is also carried unless complexed by phosphoric acid. Separation from rhenium can be achieved from sulfuric acid, but yields of technetium are can be very poor because of its reduction by trace impurities in the acid. Much more reproducible results can be obtained in the presence of an oxidizing agent, but ruthenium tetroxide (RuO_4) also distills under these conditions. It can be removed, however, by precipitation as ruthenium dioxide RuO_2. In distillation from sulfuric acid-water mixtures, technetium distills in the low-boiling point aqueous fraction, probably as pertechnetic acid. Technetium and rhenium are separated from sulfuric-hydrochloric acid mixtures; pertechnate is reduced to non-volatile Tc (IV) and remains in the acid solution. Technetium heptoxide can be separated from molybdenum trioxide by fractional sublimation at temperatures ≥ 300 °C.

ELECTRODEPOSITION. Technetium can be electrodeposited as its dioxide (TcO_2) from 2 M sodium hydroxide. The metal is partially separated from molybdenum and rhenium, but deposition only occurs from low technetium concentrations. Carrier-free ^{95}Tc and ^{96}Tc have been electrolyzed on a platinum electrode from dilute sulfuric acid. Optimum electroplating of technetium has been achieved at pH 5.5 in the presence of very dilute fluoride ion. Yields were better with a copper electrode instead of platinum—about 90 percent was collected in two hours. Yields of 98-99 percent were achieved for platinum electrodes at pH 2-5 when the plating time of up to 20 hours was used. In 2 M sulfuric acid containing traces of fluoride, metallic technetium instead of the dioxide is deposited on the electrode.

Methods of Analysis

^{99}Tc is analyzed by ICP-MS or from its beta emission. No gamma rays are emitted by this radionuclide. For ICP-MS analysis, technetium is stripped from an extraction chromatography resin and measured by the spectral system. The results should be corrected for interference by ^{99}Ru, if present. For beta analysis, technetium can be electrodeposited on a platinum disc and beta counted. Alternatively, it is collected by extraction-chromatography techniques. The resin from a column or the disc from a filtration system is placed in a liquid scintillation vial and counted. ^{99m}Tc ($t_{1/2}$=6.0h), measured by gamma-ray spectrometry, can be used as a tracer for measuring the chemical yield of ^{99}Tc procedures. Beta emission from the tracer should then be subtracted from

the total beta count when measuring ^{99}Tc. Alternatively, samples are counted immediately after isolation and concentration of technetium to determine the chemical recovery, then the ^{99m}Tc is allowed to decay before analysis of the ^{99}Tc. A widely used medical application is the technetium generator. ^{98}Mo is neutron irradiated and chemically oxidized to $^{99}MoO_4^{2-}$. This solution is ion exchange onto an acid-washed alumina column. After about 1.25 days, the activity of ^{99m}Tc has grown-in to its maximum concentration. The ^{99}Tc is eluted with a 0.9% solution of NaCl, while the ^{99}Mo remains on the column. The column may have its ^{99m}Tc removed after another 1.25 days, but at a slightly smaller concentration. The ^{99m}Tc thus separated is carrier free. This process historically was referred to as "milking," and the alumina column was call the "cow."

Compiled from: Anders, 1960; CRC, 1998-99; Choppin et al., 1995; Cobble, 1964; Considine and Considine, 1983; Coomber, 1975; Cotton and Wilkinson, 1988; DOE, 1990 and 1997, 1995, 1997; Ehmann and Vance, 1991; Fried, 1995; Greenwood and Earnshaw, 1984; Hassinsky and Adloff, 1965; Kleinberg et al., 1960; Lindsay, 1988; SCA, 2001; and Wahl and Bonner, 1951.

14.10.9.9 Thorium

Thorium, with an atomic number of 90, is the second member in the series of actinide elements. It is one of only three of the actinides—thorium, protactinium, and uranium—that occur in nature in quantities sufficient for practical extraction. In solution, in all minerals, and in virtually all compounds, thorium exists in the +4 oxidation state; it is the only actinide exclusively in the +4 state in solution.

Isotopes

There are 24 isotopes of thorium ranging inclusively from ^{213}Th to ^{236}Th; all are radioactive. ^{232}Th, the parent nuclide in the natural decay series, represents virtually 100 percent of the thorium isotopes in nature, but there are a trace amounts of ^{227}Th, ^{228}Th, ^{230}Th, ^{231}Th, and ^{234}Th. The remaining isotopes are artifacts. The most important environmental contaminants are ^{232}Th and ^{230}Th, (a member of the ^{238}U decay series). They have half-lives of 1.41×10^{10} years and 75,400 years, respectively.

Occurrence and Uses

Thorium is widely but sparsely dispersed in the Earth's crust. At an average concentration of approximately 10 ppm, it is over three times as abundant as uranium. In the ocean and rivers, however, its concentration is about one-thousandth that of uranium (about 10^{-8} g/L) because its

compounds are much less soluble under environmental conditions. There are six minerals whose essential element is thorium; thorite (uranothorite) and thorianite are common examples. Several lanthanum and zirconium minerals are also thorium-bearing minerals; examples include monazite sand and uraninite. In each mineral, thorium is present as its oxide, thorium dioxide (ThO_2). Monazite sand is the most common commercial mineral, but thorite is also a source of thorium.

Thorium is extracted from its minerals with hot sulfuric acid or hot concentrated alkali, converted into thorium nitrate [$Th(NO_3)_4$] (its chief commercial compound), extracted with organic solvents (commonly kerosene containing tributylphosphate), stripped from the organic phase by alkali solutions, and crystallized as thorium nitrate or precipitated with oxalate. The metal can be produced by electodeposition from the chloride or fluoride dissolved in fused alkali halides or by thermoreduction of thorium compounds by calcium (1,000–1,200 °C). Thorium can also be produced as a by-product in the production of other valuable metals such as nickel, uranium, and zirconium, in addition to the lanthanides. Unextracted minerals or partially extracted mill tailings represent some forms of thorium contaminants found in the environment. Very insoluble forms of thorium hydroxide [$Th(OH)_4$] are other common species found.

Metallic thorium has been used as an alloy in the magnesium industry and as a deoxidant for molybdenum, iron, and other metals. Because of its high density, chemical reactivity, poor mechanical properties, and relatively high cost, it is not used as a structural material. Thorium dioxide is a highly refractory material with the highest melting point among the oxides, 3,390 °C. It has been used in the production of gas mantles, to prevent crystallization of tungsten in filaments, as furnace linings, in nickel alloys to improve corrosion resistance, and as a catalyst in the conversion of methanol to formaldehyde. ^{232}Th is a fuel in breeder reactors. The radionuclide absorbs slow neutrons, and with the consecutive emission of two beta particles, it decays to ^{233}U, a fissionable isotope of uranium with a half-life of 159,000 years.

Solubility of Compounds

Thorium exists in solution as a highly charged ion and undergoes extensive interaction with water and with many anions. Few of the compounds are water soluble; soluble thorium compounds include the nitrate [$Th(NO_3)_4$], sulfate [$Th(SO_4)_2$], chloride ($ThCl_4$), and perchlorate [$Th(ClO_4)_4$]. Many compounds are insoluble in water and are used in the precipitation of thorium from solution, including the hydroxide [$Th(OH)_4$], fluoride (ThF_4), iodate [$Th(IO_3)_4$], oxalate [$Th(C_2O_4)_2$], phosphate [$Th_3(PO_4)_4$], sulfite [$Th(SO_3)_2$], dichromate [$Th(Cr_2O_7)_2$], potassium hexafluorothorionate [K_2ThF_6], thorium ferrocyonide (II) [$ThFe(CN)_6$], and thorium peroxide sulfate [$Th(OO)_2SO_4$].

The thorium ion forms many complex ions, chelates, and solvated species that are soluble in organic solvents. This property is the basis of many procedures for the separation and purification of thorium (see below). For example, certain ions, such as nitrate and sulfate, form large unsolvated complex ions with thorium that are soluble in organic solvents. Chelates of 1,3-diketones, such as acetylacetone (acac) and 2-thenoyltrifluoroacetone (TTA), form neutral molecular chelates with the thorium ion that are soluble. In addition, many neutral organic compounds have strong solvating properties for thorium, bonding to the thorium ion in much the same way water solvates the ion at low pH. Tributylphosphate (TBP), diethyl ether, methyl ethyl ketone, mesityl oxide, and monoalkyl and dialkyl phosphates are examples of such compounds.

Review of Properties

Thorium is the first member of the actinide series of elements that includes actinium (Ac), uranium, and the transuranium elements. Thorium is a bright, silver-white metal with a density above 11 g/cm^3. It tarnishes in air, forming a dark gray oxide coating. The massive metal is stable, but in finely divided form and as a thin ribbon it is pyrophoric and forms thorium oxide (ThO_2). Thorium metal dissolves in hydrochloric acid, is made passive by nitric acid, but is not affected by alkali. It is attacked by hot water and steam to form the oxide coating and hydrogen, but its reactions with water are complicated by the presence of oxygen. Thorium has four valence electrons ($6d^27s^2$). Under laboratory conditions, chlorides, bromides, and iodides of the bi- and trivalent state have been prepared. In aqueous solution and in most compounds, including all those found in nature, thorium exists only in the +4 oxidation state; its compounds are colorless in solution unless the anion provides a color. Thorium forms many inorganic compounds in acid solution.

Solution Chemistry

Because the only oxidation state of thorium in solution is the +4 state, its chemistry is not complicated by oxidation-reductions reactions that might produce alternate species in solution. With the +4 charge and corresponding charge-to-radius ratio of 4.0, however, thorium forms very stable complex ions with halides, oxygen-containing ligands, and chelating agents. Although Th^{+4} is large (0.99 Å; 0.099 nm; 99 pm) relative to other +4 ions (Ti, Zr, Hf, Ce) and therefore more resistant to hydrolysis, as a highly charged ion, it hydrolyzes extensively in aqueous solutions above pH 3 and tends to behave more like a colloid than a true solution. The concentration of Th^{+4} is negligible under those conditions. Below pH 3, however, the uncomplexed ion is stable as the hydrated ion, $Th(H_2O)_{8\text{ or }9}^{+4}$.

COMPLEXATION. Thorium has a strong tendency to form complex ions in solution. The presence of HF forms very stable complex ions, for example, with one, two, or three ligands:

$$Th^{+4} + HF \rightarrow ThF^{+3} + H^{+1}$$
$$ThF^{+3} + HF \rightarrow ThF_2^{+2} + H^{+1}$$
$$ThF_2^{+2} + HF \rightarrow ThF_3^{+1} + H^{+1}$$

These complex ions represent the predominant species in solutions containing HF. Stable complex ions also form with oxygen-containing ligands such as nitrate, chlorate, sulfate, bisulfate, iodate, carbonate, phosphate, most carboxylate anions, and chelate anions. Some chelating agents such as salicylate, acetylacetonate (acac), theonyltrifluoroacetonate (TTA), and cupferron form complexes that are more soluble in organic solvents, This property is the basis of several radiochemical isolation methods for thorium. Through the formation of soluble complex ions, chelating agents found in some industrial wastewater or natural water samples will interfere to varying degrees with the isolation of thorium by ferric hydroxide [$Fe(OH)_3$] coprecipitation. Alternative isolation methods should be used, such as coprecipitation from an acidic solution with an alternative reagent. Protonation of the anionic form of chelates with acid renders them useless as chelating agents. Other complexing agents also interfere with precipitation by the formation of soluble ions. Thorium, for example, does not precipitate with oxalate in the presence of carbonate ions. A procedure for separating thorium from rare-earth ions takes advantage of the formation of a soluble thorium-EDTA complex that inhibits thorium precipitation when the rare-earth ions are precipitated with phosphate. The presence of high concentrations of other complexing agents such as phosphate, chloride, and other anions found in some samples takes thorium into a completely exchangeable form when it is solubilized in high-concentration nitric acid.

HYDROLYSIS. Beginning at pH 3, thorium ions undergo extensive hydrolysis to form monomeric and polymeric complexes in solution, leaving little (approximately 5×10^{-6} M) Th^{+4} in a saturated solution at pH 3. Tracer solutions containing ^{234}Th can be added at pH 2 to allow equilibration because it is not likely to occur if part of the thorium is hydrolyzed and bound in polymeric forms.

The hydrolysis process is complex, depending on the pH of the solution and its ionic strength. Several species have been proposed: three are polynuclear species, $Th_2(OH)_2^{+6}$, $Th_4(OH)_8^{+8}$, and $Th_6(OH)_{15}^{+9}$; and two are monomeric species, $Th(OH)^{+3}$ and $Th(OH)_2^{+2}$. The monomeric species are of minor importance except in extremely dilute solutions, but they become more important as the temperature increases. The presence of chloride and nitrate ion diminishes hydrolysis, because the formation of corresponding complex ions markedly suppresses the process.

Hydrolysis increases with increasing hydroxide concentration (pH), and eventually polymerization of the species begins. At a pH of about 5, irreversible hydrolysis produces an amorphous precipitate of thorium hydroxide, a polymer that might contain more than 100 thorium atoms. Just before precipitation, polymerization slows and equilibration might take weeks or months to obtain.

Routine fuming of a sample containing organic material with nitric acid is recommended after addition of tracer, but before separation of thorium as a hydroxide precipitate because there is evidence for lack of exchange between added tracer and isotope already in solution. Complexing with organic substances in the initial solution or existence of thorium in solution as some polymeric ion have been suggested as the cause.

ADSORPTION. The insoluble hydroxide that forms in solution above pH 3 has a tendency to coagulate with hydrated oxides such as ferric oxide. The high charge of the thorium cation (+4), high charge-to-radius ratio, and tendency to hydrolyze all contribute to the ability of thorium to adsorb on surfaces by ion-exchange mechanisms or chemical adsorption mechanisms. These adsorption properties greatly affect the interaction of thorium with ion-exchange resins and environmental media such as soil.

Dissolution of Samples

Thorium samples are ignited first to remove organic materials. Most compounds will decompose when sintered with sodium peroxide (Na_2O_2), and most thorium minerals will yield to alternate sodium peroxide sintering and potassium pyrosulfate ($K_2S_2O_7$) fusion. It is often necessary to recover thorium from hydrolysis products produced by these processes. The hydrolysis products are treated with hydrofluoric acid, and thorium is recovered as the insoluble fluoride. Rock samples are often dissolved in hydrofluoric acid containing either nitric acid or perchloric acid. Monazite is dissolved by prolonged sintering or with fuming perchloric or sulfuric acid. Thorium alloys are dissolved in two steps, first with aqua regia (nitric and hydrochloric acid mixture) followed by fusion with potassium pyrosulfate. Thorium targets are dissolved in concentrated nitric acid containing hydrofluoric acid, mantles in nitric or sulfuric acid, and tungsten filaments with aqua regia or perchloric acid.

Separation Methods

PRECIPITATION AND COPRECIPITATION. Precipitation and coprecipitation are used to separate and collect thorium from aqueous solutions either for further treatment in an analytical scheme or for preparation of a sample for counting. Formation of insoluble salts is used to precipitate thorium

from solution; examples include the hydroxide, peroxide, fluoride, iodate, oxalate, and phosphate, among others. Tracer quantities of thorium are commonly coprecipitated with lanthanum fluoride (LaF_3), neodymium fluoride (NdF_3), and cerium fluoride (CeF_3) in separation schemes and to prepare samples for alpha counting. Tracer quantities are also carried with calcium oxalate [$Ca(C_2O_4)$], ferric hydroxide [$Fe(OH)_3$], zirconium iodate ($ZrIO_4$), zirconium phosphate (Zr_3PO_4), and barium sulfate ($BaSO_4$).

ION EXCHANGE. The highly charged thorium cation is strongly adsorbed onto cation exchangers and is more difficult to elute than most other ions. Its strong adsorption property makes it possible to remove trace quantities of thorium from a large volume of solution onto small amounts of ion-exchange resin. Washing the resin with mineral acids of various concentrations separates thorium from less strongly bound cations that elute from the resin. For example, Th^{+4} remains bonded at all hydrochloric concentrations, allowing other cations to be eluted at different concentrations of acid. Thorium is eluted by complexing agents such as citrate, lactate, fluoride, carbonate, sulfate, or oxalate that reduce the net charge of the absorbing species, causing reversal of the adsorption process.

Anion exchangers are useful for separating thorium, but the contrasting behavior of thorium with the resin depends on whether hydrochloric or nitric acid is used as an eluent. In hydrochloric acid, several metal ions, unlike thorium, form negative complexes that can be readily removed from a thorium solution by adsorption onto the anionic exchanger. Thorium forms positively charged chlorocation complexes or neutral thorium chloride ($ThCl_4$) in the acid and is not adsorbed by the resin at any hydrochloric acid concentration. In contrast, thorium forms anionic complexes in nitric acid solution that adsorb onto the exchanger over a wide range of nitric acid concentrations, reaching a maximum affinity near 7 M nitric acid. Behavior in nitric acid solution is the basis for a number of important radiochemical separations of thorium from rare earths, uranium, and other elements.

ELECTRODEPOSITION. Thorium separated from other actinides by chemical methods can be electrodeposited for alpha counting from a dilute solution of ammonium sulfate adjusted to a pH of 2. The hydrous oxide of thorium is deposited in one hour on a highly polished platinum disc serving as the cathode of an electrolytic cell. The anode is a platinum-iridium alloy.

SOLVENT EXTRACTION. Many complexes and some compounds of thorium can be extracted from aqueous solutions into a variety of organic solvents. The TTA (α-theonyltrifluoroacetone) complex of metals is widely used in radiochemistry for the separation of ions. Thorium can be separated from most alkali metal, alkaline earth, and rare earth metals after the complex is

quantitatively extracted into benzene above pH 1. Backwashing the organic solution with dilute acid leaves the more soluble ions in benzene.

Extraction of nitrates and chlorides of thorium into organic solvents from the respective acid solutions is widely used for isolation and purification of the element. One of the most common processes is the extraction of thorium nitrate from a nitric acid solution with TBP (triisobutyl-phosphate). TBP is usually diluted with an inert solvent such as ether or kerosene to reduce the viscosity of the mixture. Dilution reduces the extraction effectiveness of the mixture, but the solubility of many contaminating ions is greatly reduced, increasing the effectiveness of the separation when the thorium is recovered by backwashing.

Long-chain amine salts have been very effective in carrying thorium in laboratory and industrial extraction process using kerosene. Complex sulfate anions of thorium are formed in sulfuric acid that act as the counter ion to the protonated quaternary amine cation. They accompany the organic salt into the organic phase.

In recent years, solvent extraction chromatography procedures have been developed to separate thorium. These procedures use extraction chromatography resins that consist of extractant materials such as CMPO in TBP or DPPP (dipentylpentylphosphonate), also called DAAP (diamylamylphosphonate), absorbed onto an inert polymeric material. They are used in a column, rather than in the traditional batch mode, and provide a rapid efficient method of separating the radionuclide with the elimination of large volumes of organic waste.

Methods of Analysis

Chemical procedures are used for the analysis of macroscopic quantities of thorium in solution after it has been separated by precipitation, ion exchange, extraction, and/or extraction chroma-tography from interfering ions. Gravimetric determination generally follows precipitation as the oxalate that is calcined to the oxide (ThO_2). Numerous volumetric analyses employ EDTA as the titrant. In the most common spectrometric method of analysis, thorin, a complex organoarsenic acid forms a colored complex with thorium that is measured in the visible spectrum.

Trace quantities of thorium are measured by alpha spectrometry after chemical separation from interfering radionuclides. ^{227}Th, ^{228}Th, ^{230}Th, and ^{232}Th are determined by the measurement of their respective spectral peaks (energies), using ^{234}Th as a tracer to determine the chemical yield of the procedure. The activity of the tracer is determined by beta counting in a proportional counter. ^{234}Th also emits gamma radiation that can be detected by gamma spectrometry; however, the peak can not be measured accurately because of interfering peaks of other gamma-emitting

radionuclides. ^{229}Th is sometimes used as a tracer to determine the chemical yield of the alpha spectrometric procedure, but it produces considerable recoil that might contaminate the detector.

Compiled from: Ahrland, 1986; Baes and Mesmer, 1976; Cotton, 1991; Cotton and Wilkinson, 1988; DOE, 1990 and 1997, 1997; EPA, 1980 and 1984; Greenwood, 1984; Grimaldi, 1961; Hassinsky and Adloff, 1965; Hyde, 1960; Katzin, 1986; Lindsey, 1988.

14.10.9.10 Tritium

Unlike the elements reviewed in this section, tritium the only radionuclide of the element hydrogen. It contains two neutrons and is represented by the symbols ^{3}H, ^{3}T, or simply, T. The atom contains only one valence electron so its common oxidation state, besides zero, is +1, although it can exist in the -1 state as a metal hydride.

Occurrence and Uses

Tritium is found wherever stable hydrogen is found, with and without the other isotopes of the element (hydrogen and deuterium)—as molecular hydrogen (HT, DT, T_2), water (HTO, DTO, T_2O), and inorganic and organic compounds, hydrides and hydrocarbons, respectively, for example. About 99 percent of the radionuclide in nature from any source is in the form of HTO. Natural processes account for approximately one T atom per 10^{18} hydrogen atoms. The source of some natural tritium is ejection form the sun, but the primary source is from bombardment of ^{14}N with cosmic neutrons in the upper atmosphere:

$$^{14}_{7}N + ^{1}_{0}n \rightarrow ^{3}H + ^{12}_{6}C$$

Most tritium from this source appears as HTO.

Tritium is produced in laboratory and industrial processes by nuclear reactions such as:

$$^{2}_{1}D + ^{2}_{1}D \rightarrow ^{3}_{1}T + ^{1}_{1}H$$

For large-scale production of tritium, ^{6}Li alloyed with magnesium or aluminum is the target of neutrons:

$$^{6}_{3}Li + ^{1}_{0}n \rightarrow ^{3}_{1}T + ^{4}_{2}He$$

The radionuclide is retained in the alloy until released by acid dissolution of the target. Large quantities are handled as HT or HTO. HTO is formed from HT when it is exposed to oxygen or water vapor. A convenient way to store tritium is as the hydride of uranium (UT_3). It is formed by reacting the gas with finely divided uranium and is released by heating the compound above 400 °C.

Tritium is also produced in nuclear reactors that contain water or heavy water from the neutron bombardment of deuterium:

$$^{2}D + ^{1}_{0}n \rightarrow ^{3}T$$

Most tritium (>99%) in reactors is formed from the fission process as a ternary particle. The main use for tritium is in fission bombs to boost their yield and in thermonuclear weapons, the hydrogen bomb. Tritium bombarded with high-energy deuterons undergoes fusion to form helium and releasing neutrons:

$$^{3}_{1}H + ^{2}_{1}H \rightarrow ^{4}_{2}He + ^{1}_{0}n$$

A tremendous amount of energy is released during the nuclear reaction, much more than the energy of the bombarding particle. Fusion research on controlled thermonuclear reactions should lead to an energy source for electrical generation.

Tritium absorbed on metals are a source of neutrons when bombarded with deuterons. Mixed with zinc sulfide, it produces radioluminescence that is used in luminescent paint and on watch dials. Gaseous tritium in the presence of zinc sulfide produces a small, permanent light source found in rifle sights and exit signs. Tritium is also a good tracer since it does not emit gamma radiation. Hydrological studies with HTO is used to trace geological water and the movement of glaciers. It is also used as a tracer for hydrogen in chemical studies and biological research. In medicine, it is used for diagnosis and radiotreatment.

Review of Properties

Tritium decays with a half-life of 12.3 y by emission of a low-energy beta particle to form ^{3}He, and no gamma radiation is released. The range of the beta particle is low, 6 mm in air and 0.005 mm in water or soft tissue.

The physical and chemical properties of tritium are somewhat different than hydrogen or deuterium because of their mass differences (isotope effects). Tritium is approximately twice as

heavy as deuterium and three times heavier than hydrogen, and the isotope effect can be large for mass differences of these magnitudes. In its simple molecular form, tritium exists primarily as T_2 or DT. The oxide form is HTO, DTO, or T_2O, with higher molecular weights than water (H_2O). Thus molecules of tritiated water are heavier, and any process such as evaporation or distillation that produces a phase transition results in isotopic fractionation and enrichment of tritium in water. In a mixture of the oxides, various mixed isotopic water species are generally also present because of exchange reactions: in any mixture of H_2O, D_2O, and T_2O, HTO and DTO are found.Molecules of HTO are more stable than H_2O or HDO and are not as easily decomposed by electrolysis, to form hydrogen or oxygen. Electrolysis of a water sample to about five percent of its original volume, therefore, concentrates tritium by retaining approximately 80 percent of the tritium from the initial volume. Reaction rates of chemical bonds containing tritium are slower because of the isotope effect than those of hydrogen. The rates can be as small as 1:64 (T:H), and these differences should be considered when interpreting tracer studies of reaction mechanisms. Chemical isotope effects are large in some biological systems. Some algae and bacteria selectively exchange hydrogen isotopes, and the preference is tritium over deuterium over hydrogen. Enrichment of tritium can be about 2.5.

Tritium can be introduced into organic compounds by exposing T_2 to the compound for a few days or weeks, irradiation of the compound and a lithium salt with neutrons (recoil labeling), or it can be selectively introduced into a molecule by chemical synthesis using a molecular tritium source such as HTO. Beta radiation causes exchange reactions between hydrogen atoms in the compound and tritium and migration of the isotope within the molecule. Phenol (C_6H_5OH), for example, labeled with tritium on the oxygen atom (C_6H_5OT) will become C_6H_4TOH and C_6H_4TOT. When tritium samples are stored in containers made from organic polymers such as polyethylene, the container will adsorb tritium, resulting in a decrease in the concentration of tritium in the sample. Eventually, the tritium atoms will migrate to the outer surface of the container, and tritium will be lost to the environment. Catalytic exchange also occurs in tritiated solutions or solutions containing T_2 gas. Exchange is very rapid with organic compounds when H^{+1} or OH^{-1} ions or if a hydrogen-transfer agent such as Pt or Pd is present.

Tritium as HT or HTO will absorb on most metallic surfaces. Penetration at room temperature is very slow, and the radionuclide remains close to the surface. In the form of HTO, it can be removed with water, or by hydrogen gas in the form of HT. Heating aids the removal. When tritium is absorbed at elevated temperatures, it penetrates deeper into the surface. Adsorption under these conditions will result in enough penetration to cause structural damage to the metal, especially if the process continues for extended periods. Hydrogenous material such as rubber and plastics will also absorb tritium. It will penetrate into the material, and hydrogenous materials are readily contaminated deep into the material, and it is impossible to completely

remove the tritium. Highly contaminated metal or plastic surfaces can release some of the loosely bound tritium immediately after exposure in a process called outgassing.

Pure T_2O can be prepared by oxidation of tritium gas with hot copper(II) oxide or direct combination of the gas with oxygen in the presence of an electrical spark. It is never used for chemical or biological processes because one milliliter contains 2,650 curies. The liquid is self-luminescent, undergoes rapid self-radiolysis, and considerable radiation damage is done to dissolved species. For the same reason, very few compounds of pure tritium have ever been prepared or studied.

The radiotoxity of tritium is rated medium. Tritium is not a hazard outside the body. Gamma radiation is not released by its decay. The beta emission is low in energy compared to most beta emitters and readily stopped by the outer layer of skin. Only ingested tritium can be a hazard. Exposure to tritium is primarily in the form of HT gas or HTO water vapor, although T_2 and T_2O may be present. Only about 0.005 percent of the activity of inhaled HT gas is incorporated into lung tissue, and most is exhaled. Tritiated water vapor, however, is almost 100 percent absorbed from inhalation or ingestion. In addition, tritiated water can be absorbed through the skin or wounds. Not all gloves will prevent exposure because of the ability of tritium to be absorbed by the gloves themselves. Tritium is found in tissue wherever hydrogen is found. The biological half-life is about ten days, but the value varies significantly, depending on exertion rates and fluid intake.

Environmental tritium is formed in the gaseous and aqueous forms, but over 99 percent of tritium from all sources is found in the environment after exchange with hydrogen in water in the form of HTO. It is widely distributed in the surface waters of the earth and makes a minor contribution to the activity of ocean water. It can also be found in laboratories and industrial sites in the form of metal hydrides, tritiated pump oil, and tritiated gases such as methane and ammonia.

Separation Methods

DISTILLATION. Tritium in water samples is essentially in the form of HTO. It can be removed quantitatively from aqueous mixtures by distillation to dryness, which also separate it form other radionuclides. Volatile iodine radionuclides are precipitated as silver iodide before distillation, if they are present. The aqueous solution is usually distilled, however, from a basic solution of potassium permangenate, which will oxidize radionuclides, such as iodine and carbon, and oxidize organic compounds that might interfere with subsequent procedures, liquid scintillation counting, for example. Charcoal can also be added to the distillation mixture as an additional measure to remove organic material. Contaminating tritium in soil samples can be removed by

distillation from similar aqueous mixtures. All tritium in soil samples might not be recovered by this method, however, if the tritium is tightly bound to the soil matrix. Tritium also can be removed by distillation of an azeotrope mixture formed with toluene or cyclohexane. In some procedures, tritium is initially separated by distillation and then concentrated (enriched) by electrolysis in an acid or base solution. Recovery of tritium from the electrolytic cell for analysis is accomplished by a subsequent distillation.

DECOMPOSITION. Organically bound tritium (OBT) in vegetation, food, and tissue samples can be removed by combustion. The sample is freeze dried (lyophilized), and the water from the process is collected in cold traps for tritium analysis. The remaining solid is collected as a pellet, which is burned at 700 °C in a highly purified mixture of argon and oxygen in the presence of a copper(I) oxide (CuO) catalyst, generated on a copper screen at the temperature of the process. Water from the combustion process, containing tritium from the pellet, and water from the freeze-drying process is analyzed for tritium by liquid scintillation counting.

Tritium in HTO can be reduced to TH by heating with metals, such as magnesium, zinc, or calcium, and analyzed as a gas.

CONVERSION TO ORGANIC COMPOUNDS. Compounds that react readily with water to produce hydrogen derivatives can be used to isolate and recover tritium that is present in the HTO form. Organic compounds containing magnesium (Grignard reagents) with relatively low molecular-weights will react spontaneously with water and produce a gaseous product containing hydrogen from the water. Tritium from HTO in a water sample will be included in the gaseous sample. It is collected after formation by condensation in a cold trap and vaporized into a gas tube for measurement. Grignard reagents formed from butane, acetylene, and methane can be used in this method. Tritiated butane is produced by the following chemical reaction:

$$C_4H_9MgBr + THO \rightarrow C_4H_9T + Mg(OH)Br$$

Inorganic compounds can also be use to produce gaseous products:

$$Al_4C_3 + 3\ HTO + 9\ H_2O \rightarrow 3\ CH_3T + 4\ Al(OH)_3$$

EXCHANGE. Methods to assess tritium in compounds take advantage of exchange reactions to collect the radionuclide in a volatile substance that can be collected in a gas tube for measurement. Acetone is one compound that easily exchanges tritium in an acid or base medium and is relatively volatile.

Methods of Analysis

Tritium is collected primarily as HTO along with water (H_2O) by distillation and then determined from its beta emission in a liquid scintillation system. No gamma rays are emitted. The distillation process is usually performed from a basic solution of potassium permangenate to oxidize radionuclides and organic compounds, preventing them from distilling over and subsequently interfering with counting. Charcoal can also be added to the distillation mixture as an additional measure to remove organic material. Volatile iodine radionuclides can be precipitated as silver iodide before distillation.

Compiled from: Choppin et al., 1995; Cotton and Wilkinson, 1988; DOE, 1994; Duckworth, 1995; Greenwood and Earnshaw, 1984; Hampel, 1968; Hassinky and Adloff, 1965; Kaplan, 1995; Lindsay, 1988; Mitchell, 1961; Passo and Cook, 1994.

14.10.9.11 Uranium

Uranium, atomic number 92, is the last naturally occurring member of the actinide series and the precursor to the transuranic elements. Three isotopes are found in nature, and uranium was the active constituent in the salts whose study led to the discovery of radioactivity by Becquerel in 1896.

Isotopes

There are 19 isotopes of uranium with mass numbers ranging from 222 to 242. All isotopes are radioactive with half-lives range ranging from microseconds to billions of years. ^{235}U (0.72%) and ^{238}U (99.27%) are naturally occurring as primordial uranium. ^{234}U has a natural abundance of 0.0055%, but is present as a part of the ^{238}U decay natural decay chain. The ^{234}U that was formed at the time the earth was formed has long since decayed. The half-lives of these principal isotopes of uranium are listed below.

Isotope	Alpha Decay Half-Life	Spontaneous Fission Half-Life
234	2.46×10^5 years	1.42×10^{16} years
235	7.04×10^8 years	9.80×10^{18} years
238	4.48×10^9 years	8.08×10^{15} years

These isotopes have two different decay modes. Each decay mode has its own characteristic half-life. As seen above the alpha decay mode is the most significant, since it has the shortest half-life for each of these isotopes.

Another isotope of uranium of significance is ^{232}U (half-life 69.8 years). It is used as a tracer in uranium analyses and is also an alpha emitter so it can be determined concurrently with the major uranium isotopes by alpha spectrometry.

^{235}U and artificially produced ^{233}U are fissionable material on bombardment with slow (thermal) neutrons. Other uranium radionuclides are fissionable with fast moving neutrons, charged particles, high-energy photons, or mesons. ^{238}U and ^{235}U are both parents of natural radioactive decay series, the uranium series of ^{238}U that eventually decays with alpha and beta emissions to stable ^{206}Pb and the actinium series of ^{235}U that decays to ^{207}Pb.

Occurrence and Uses

Naturally occurring uranium is believed to be concentrated in the earth's crust with an average concentration of approximately 4 ppm. Granite rocks contains up to 8 ppm or more, and ocean water contains 0.0033 ppm. Many uranium minerals have been discovered. Among the better known are uraninite, carnotite, adavidite, pitchblende, and coffinite. The latter two minerals are important commercial sources of uranium. It is also found in phosphate rock, lignite, and monazite sands and is commercially available from these sources. The artificial isotope, ^{233}U, is produced from natural ^{232}Th by absorption of slow neutrons to form ^{233}Th, which decays by the emission of two beta particles to ^{233}U.

Uranium is extracted from uranium minerals, ores, rocks, and sands by numerous chemical extraction (leaching) processes. The extraction process is sometimes preceded by roasting the ore to improve the processing characteristic of the material. The extraction process uses either an acid/oxidant combination or sodium carbonate treatment, depending on the nature of the ore, to convert the metal to a soluble form of the uranyl ion. Uranium is recovered from solution by precipitating the uranate salt with ammonia or sodium hydroxide solution. Ammonium uranate is know as yellow cake. The uranate salt is solubilized to give a uranyl nitrate solution that is further purified by extraction into an organic phase to separate the salt from impurities and subsequent stripping with water. It is precipitated as a highly purified nitrate salt that is used to produce other uranium compounds—uranium trioxide (UO_3) by thermal processing or uranium dioxide (UO_2) on reduction of the trioxide with hydrogen. Uranium tetrafluoride (UF_4) is prepared, in turn, form the dioxide by treatment with hydrogen fluoride. The metal is recovered

by fused-salt electrolysis in molten sodium chloride-calcium chloride or reduction with more active metals such as calcium or magnesium (Ames Process) in an inert atmosphere at 1,000 °C.

Early in the twentieth century, the only use of uranium was in the production of a brown-yellow tinted glass and glazes; it was a byproduct of the extraction of radium, which was used for medicinal and research purposes. Since the mid-twentieth century, the most important use of uranium is as a nuclear fuel, directly in the form of ^{233}U and ^{235}U, fissionable radionuclides, and in the form of ^{238}U that can be converted to fissionable ^{239}Pu by thermal neutrons in breeder reactors. Depleted uranium, uranium whose ^{235}U content has been reduced to below about 0.2 percent, the majority of waste from the uranium enrichment process, is used in shielded containers to transport radioactive materials, inertial guidance devices, gyro compasses, counterweights for aircraft control surfaces, ballast for missile reentry vehicles, fabrication of armor-piercing conventional weapons, and tank armor plating. Uranium metal is used as a X-ray target for production of high-energy X-rays, the nitrate salt as a photographic toner, and the acetate is used in analytical chemistry.

Solubility of Compounds

Only a small number of the numerous uranium compounds are soluble in water. Except for the fluorides, the halides of uranium (III and IV) are soluble, as are the chloride and bromide of uranium (V) [UOX_2] and the fluoride, chloride, and bromide of uranium (VI) [UO_2X_2]. Several of the uranyl (UO_{2+2}) salts of polyatomic anions are also soluble in water: the sulfate, bicarbonate, acetate, thiocyanate, chromate, tungstate, and nitrate. The latter is one of the most water-soluble uranium compounds.

Review of Properties

Uranium is a dense, malleable and ductile metal that exists in three allotropic forms: alpha, stable to 688 °C where it forms the beta structure, which becomes the gamma structure at 776 °C. It is a poor conductor of electricity. The metal absorbs gases and is used to absorb tritium. Uranium metal tarnishes readily in an oxidation process when exposed to air. It burns when heated to 170 °C, and the finely divided metal is pyrophoric. Uranium slowly decomposes water at room temperature, but rapidly at 100 °C. Under a flux of neutrons and other accelerated particles, atoms of uranium are displaced from their equilibrium position in its metallic lattice. With high temperatures and an accumulation of fission products, the metal deforms and swells, becoming twisted, porous, and brittle. The problem can be avoided by using some of its alloys, particularly alloys of molybdenum and aluminum.

Uranium forms a large number of binary and ternary alloys with most metals. It also form compounds with many metals: aluminum, bismuth, cadmium, cobalt, gallium, germanium, gold, indium, iron, lead, magnesium, mercury, nickel, tin, titanium, zinc, and zirconium. Many binary compounds of the nonmetals are also known: hydrides, borides, carbides, nitrides, silicides, phosphides, halides, and oxides. Although other oxides are known, the common oxides are UO_2, UO_3, and U_3O_8. Uranium reacts with acids to form the +4 salts and hydrogen. It is very reactive as a strong reducing agent.

Uranium compounds are toxic at high concentrations. The physiological damage occurs to internal organs, especially the kidneys. The radioactivity of natural uranium radionuclides is not of great concern, although it is high for some artificial isotopes. Natural uranium in the environment is considered a relatively low hazard, however, because of its very long half-life and low toxicity at minute concentrations.

Uranium in nature is almost entirely in the IV and VI oxidation states. It occurs as the oxides, UO_2 and U_3O_8, in the solid state. In ground water under oxic conditions it exists as UO_2^{+2} or complexes of carbonate such as $UO_2(CO_3)_3^{-4}$. Complex formation increases its solubility under all conditions in normal groundwater and even under fairly strong reducing conditions. The amount associated with particulate matter is small in natural oxic waters. In some waters, solubility may be limited, however, by formation of an uranyl silicate species. Uranium in general is poorly absorbed on geologic media under oxic conditions, especially at moderate and high concentrations and in the presence of high carbonate concentrations. A significant adsorption occurs at pH above about 5 or 6 because of formation of hydrolytic complexes. Reduction to the IV oxidation state would increase uptake in the environmental pH range.

Solution Chemistry

The radiochemistry of uranium is complicated because of the multiple oxidation states that can exist in solution and the extensive complexation and hydrolytic reactions the ions are capable of undergoing in solution. Four oxidation states are possible: +3, +4, +5, and +6; the latter two exist as oxycations: UO_2^{+1} and UO_2^{+2}, respectively. Their stabilities vary considerably, and the +4 and +6 states are stable in solution under certain conditions; oxidation-reduction reagents are used to form and maintain these ions in solution. Each ion has different chemical properties, and those of the +4 and +6 states have been particularly exploited to stabilize, solubilize, separate, and collect uranium. The multiple possibilities of oxidation state, complexation, and hydrolysis should be carefully considered when planning any radiochemical procedures.

OXIDATION-REDUCTION BEHAVIOR. The multiple oxidation states can be exploited during separation procedures by taking advantage of their different chemical properties. Thorium can be separated from uranium, for example, by oxidizing uranium in solution to the +6 oxidation state with 30 percent hydrogen peroxide (H_2O_2) and precipitating thorium as the hydroxide; in the +6 state, uranium is not precipitated.

The U^{+3} ion is an unstable form of uranium, produced in perchlorate or chloride solutions by reduction of UO_2^{+2} electrochemically or with zinc amalgam. It is a powerful reducing agent, and is oxidized to U^{+4} by chlorine or bromine. U^{+3} is slowly oxidized by water with the release of hydrogen, and oxygen from air causes rapid oxidation. Aqueous solutions are red-brown and are stable for several days in 1 M hydrochloric acid, especially if kept cold; rapid oxidation occurs in more concentrated acid solutions.

The tetrapositive uranous ion, U^{+4}, is produced by dissolving water-soluble salts of the ion in solution, dissolving uranium metal with sulfuric or phosphoric acid, reduction of UO_2^{+1} during its disproportionation reaction, reduction of UO_2^{+2} by Cr^{+2} or Ti^{+3}, or oxidation of U^{+3}. The tetrapositive ion is green in solution. The ion is stable, but slowly oxidizes by oxygen from air to the +6 state.

The UO_2^{+1} ion (+5 state) is extremely unstable in solution and exist only as a transient species, disproportionating rapidly to U^{+4} and UO_2^{+2} according to the following reaction in the absence of complicating factors ($k=1.7 \times 10^6$):

$$2\ UO_2^{+1} + 4\ H^{+1} = UO_2^{+2} + U^{+4} + 2\ H_2O$$

Maximum stability is observed in the pH range 2–4 where the reaction is considerably slower. Solutions of UO_2^{+1} are prepared by the dissolution of UCl_5 or reduction of UO_2^{+2} ions electrochemically or with U^{+4} ions, hydrogen, or zinc amalgam.

The +6 oxidation state of uranium is generally agreed to be in the form of the dioxo or uranyl ion, UO_2^{+2}. As the only oxidation state stable in contact with air, it is very stable in solution and difficult to reduce. Because of its exceptional stability, the uranyl ion plays a central role in the radiochemistry of uranium. It is prepared in solution by the dissolution of certain water-soluble salts: nitrate, halides, sulfate, acetate, and carboxylates; by dissolution of uranium +6 compounds; and oxidation of lower-oxidation state ions already in solution, U^{+4} with nitric acid for example. Its solutions are yellow in color.

COMPLEXATION. Uranium ions form numerous complex ions, and the solution chemistry of uranium is particularly sensitive to complexing agents present. Complex-ion chemistry is very important, therefore, to the radiochemical separation and determination of uranium. Complexation, for example, provides a method to prevent the removal of uranium ions or its contaminants from solution and can influence the stability of ions in solution.

Among the oxidation states exhibited in solution, the tendency for formation of anionic complexes is:

$$U^{+4} > UO_2^{+2} > U^{+3} > UO_2^{+1},$$

while the order of stability of the anionic complexes is represented by:

fluoride > nitrate > chloride > bromide > iodide > perchlorate > carbonate > oxalate > sulfate.

Numerous organic complexes form, including citrate, tartrate, and EDTA, especially with UO_2^{+2}.

There is evidence for only a few complexes of U^{+3}, cupferron and chloride for example. In contrast, tetrapositive uranium, U^{+4}, forms complexes with a wide variety of anions, and many are stable: halides—including fluoride (up to eight ligands, UF_8^{-4})—chloride, and bromide; thiocyanate; and oxygen-donors, nitrate, sulfates, phosphates, carbonate, perchlorate, and numerous carboxylates: acetate, oxalate, tartrate, citrate, and lactate. The low charge on UO_2^{+1} precludes the formation of very stable complexes. Fluoride (from hydrogen fluoride) is notable, however, in its ability to displace oxygen from the ion, forming UF_6^{-1}—which inhibits disproportionation—and precipitating the complex ion from aqueous solution. The uranyl ion, UO_2^{+2}, readily forms stable complexes with a large variety of inorganic and carboxylate anions very similar to those that complex with U^{+4}. In addition, numerous organic ligands besides carboxylates are known that contain both oxygen and nitrogen as donor atoms. Complex-ion formation must be considered, therefore, during precipitation procedures. Precipitation of uranium ions is inhibited, for example, in solutions containing carbonate, tartrate, malate, citrate, hydroxylamine, while impurities are precipitated as hydroxides, sulfides, or phosphates. Conversely, uranium is precipitated with ammonia, while other ions are kept in solution as complexes of EDTA.

HYDROLYSIS. Some uranium ions undergo extensive hydrolysis in aqueous solution. The reactions can lead to formation of polymeric products, which form precipitates under certain conditions. The tendency of the various oxidation states toward hydrolysis, a specific case of complexation, is, therefore, in the same order as that of complex-ion formation (above).

Little data are available on the hydrolysis of U^{+3} ion because it is so unstable in solution. Qualitative evidence indicates, however, that hydrolysis is about that to be expected for a +3 ion of its size, that is, as a much weaker acid than most other metals ions of this charge. The U^{+4} ion is readily hydrolyzed in solution, but exist as the unhydrolyzed, hydrated ion in strongly acidic solutions. Hydrolysis begins at pH<1, starting with the $U(OH)^{+3}$ species. An increase in pH, several species form progressively up to $U(OH)_5^{-1}$. The $U(OH)^{+3}$ species predominates at high acidity and low uranium concentrations, and the concentration of each species increases rapidly with the temperature of the solution. In less acidic solutions and as the concentration of uranium increases, a polymeric species forms, probably $U_6(OH)_{15}^{+9}$. Hydrolytic complexes of high molecular weight probably form subsequently, culminating in precipitation. Hydrolysis of the UO_2^{+1} ion has been estimated to be very low, consistent with the properties of a large, positive ion with a single charge. Hydrolysis of UO_2^{+2} begins at about pH 3 and is fairly complicated. In very dilute solutions, the monomeric species, $UO_2(OH)^{+1}$, forms initially; but the dimerized species, $(UO_2)_2(OH)_2^{+2}$, rapidly becomes the dominant form in solution, existing in a wide range of uranium concentration and pH. As the pH increases, more complex polynuclear species become prominent. The presence of complexing agents, such as chloride, nitrate, and sulfate ions suppress hydrolysis to varying degrees.

Dissolution of Samples

Metallic uranium dissolves in nitric acid to form uranyl nitrate. Large amounts dissolve moderately rapidly, but fine turnings or powder may react violently with nitric acid vapors or nitrogen dioxide in the vapor. The presence of oxygen in the dissolution system tends to reduce the oxides. The rate of dissolution of large amounts of uranium may be increased by the addition of small amounts of sulfuric, phosphoric, or perchloric acids to the nitric acid solution. Other common mineral acids such as sulfuric, phosphoric, perchloric, hydrochloric, and hydrobromic acid are also used to dissolve uranium metal. Simple organic acids in hydrochloric acid dissolve the metal, and other solvent systems are used: sodium hydroxide and hydrogen peroxide, bromine in ethyl acetate, and hydrogen chloride in ethyl acetate or acetone. Uranium compounds are dissolved in numerous solvents and solvent combinations such as water, mineral acids, organic solvents such as acetone, alcohols, and diethyl ether. Dissolution of uranium from minerals and ores is accomplished by decomposition of the sample or leaching the uranium. Grinding and roasting the sample facilitates recovery. Decomposition of the sample can be accomplished with mineral acids or by fusion or a combination of the two processes. Hydrofluoric acid aids the process. The sample can be fused with sodium carbonate, sodium hydroxide, sodium peroxide, sodium bisulfate, ammonium sulfate, lithium metaborate, and magnesium oxide. The fused sample is dissolved in water or acid. Acid and alkaline mixtures are used to leach uranium from minerals and ores. The procedures employ common mineral acids or

alkaline carbonates, hydroxides, and peroxides. Liquid biological samples may also be extracted to remove uranium, or the solid sample can be ashed by a wet or dry process and dissolved in acid solution. Wet ashing is carries out with nitric acid and completed with perchloric acid, but extreme caution should be used when using perchloric acid in the presence of organic material.

Separation Methods

PRECIPITATION AND COPRECIPITATION. There are a large number of reagents that will precipitate uranium over a wide pH range. The number of reagents available coupled with the two possible oxidation states of uranium in solution and the complexing properties of the ions provide many opportunities to separate uranium from other cations and the two oxidation states from each other. Precipitation can be inhibited, for example, by the presence of complexing agents that form soluble complexes. Complexes that form weak complexes with uranium and strong complexes with other cations allow the separation of uranium by its precipitation while the complexed cations remain in solution. EDTA has been used in this manner to separate uranium form many of the transition metals and alkaline earths. In contrast, uranium forms a very strong soluble complex with carbonate, and this property has been used to keep uranium in solution while ammonium hydroxide precipitates iron, titanium, zirconium, and aluminum. In a similar manner, uranium is separated from other cations as they are precipitated as sulfides or phosphates. Common precipitating reagents and used for separation include: ammonium hydroxide, precipitates uranium quantitatively at pH $\geq$ 4; carbonate, which will form soluble anionic complexes with uranium (VI) at pH 5 to 11 while many other metals form insoluble hydroxides; peroxide; oxalic acid, completely precipitate uranium (IV) while uranium (VI) forms a soluble complex; iodide; iodate; phosphate for uranium (VI) over a wide pH range; sulfate; cupferron, precipitates uranium (IV) from an acidic solution but uranium (VI) from a neutral solution; and 8-hydroxyquinoline, which forms a quantitatively precipitate with uranium(VI) only.

Coprecipitation of uranium is accomplished with several carriers. In the absence of carbonate, it is quantitatively coprecipitated with ferric hydroxide at pH from 5 to 8. Aluminum and calcium hydroxide are also employed to coprecipitate uranium. Uranium (VI), however, is only partially carried by metal hydroxides in the presence of carbonate, and the amount carried decreases as the concentration of carbonate increases. Small amounts of uranium (VI) coprecipatate with ceric and thorium fluoride, calcium, zirconium, and aluminum phosphate, barium carbonate, thorium hexametaphosphate, magnesium oxide, and thorium peroxide. Uranium (IV) is carried on ceric sulfate, the phosphates of zirconium, bismuth, and thorium, lanthanum and neodymium fluoride, ceric and zirconium iodates, barium sulfate, zirconium phosphate, and bismuth arsenate.

SOLVENT EXTRACTION. Liquid-liquid extraction is the most common method for the separation of uranium in radioanalytical procedures. Extraction provides a high-recovery, one-batch process that is more reproducible than other methods. With the development of extraction chromatography, solvent extraction has become a very efficient process for uranium separation. Many and varied procedures are used to extract uranium from aqueous solutions, but the conditions can be summarized as: (1) composition of the aqueous phase (form of uranium, type of acid present, and presence of common cations and anions and of foreign anions); (2) nature of organic phase (type and concentration of solvent and diluent); (3) temperature; and (4) time of equilibrium. Extraction processes can be conveniently divided into three systems: those based on (1) oxygen bonding, (2) chelate formation, and (3) extraction of anionic complexes.

Oxygen-bonding systems are more specific than those based on chelate formation. The employ organic acids, ethers, ketones, esters, alcohols, organophosphates (phosphoesters), and nitroalkanes. Ethers are effective for the extraction of uranyl nitrate from nitric acid solutions. Cyclic ethers are especially effective, and salting agents such as calcium nitrate increase the effectiveness. Methyl isobutyl ketone (MIBK or hexone) also effectively extracts uranium as the nitrate complex. It has been used extensively by industry in the Redox process for extracting uranium and plutonium from nuclear fuels. Aluminum hydroxy nitrate [$AlOH(NO_3)_2$] is an excellent salting agent for the process and the extraction efficiency is increased by the presence of the tetrapropylammonium cation [$(C_3H_7)_4N^{+1}$]. Another common system, used extensively in the laboratory and in industrial process to extract uranium and plutonium from fission products, known as the PUREX process (plutonium uranium reduction extraction), is used in most fuel reprocessing plants to separate the radionuclides. It employs TBP, tri-*n*-butyl phosphate [$(C_4H_9)_3PO$], in a hydrocarbon solvent, commonly kerosene, as the extractant. The uranium fuel is dissolved in nitric acid, and uranium and plutonium are extracted into a 30 percent TBP solution, forming a neutral complex, $UO_2(TBP)_2$. The organic phase is scrubbed with nitric acid solution to remove impurities, plutonium is removed by back-extracting it as Pu(III) with a nitric acid solution containing a reducing agent, and uranium is removed with dilute nitric acid. A complexing agent can also be used as a stripping agent. Trioctylphosphine oxide is 100,000 times more efficient in extracting uranium (VI). In both cases, nitric acid is used both to form the uranium extracting species, uranyl nitrate, and as the salting agent. Salting with aluminum nitrate produces a higher extraction efficiency but less specificity for uranium. Specificity depends the salt used and it concentration and the diluent concentration.

Uranium is also extracted with select chelate forming agents. One of the most common systems used for uranium is cupferron in diethyl ether or chloroform. Uranium (VI) is not extracted from acidic media, so impurities soluble in the mixture under acidic conditions can be extracted first.

Uranium (VI) can be reduced to uranium (IV) for subsequent extraction. Other chelating agents used to extract uranium include 8-hydroxyquinoline or acetylacetone in hexone or chloroform.

Amines with molecular weights in the 250 to 500 range are used to extract anionic complexes of uranium (VI) from acidic solutions. The amine forms a salt in the acidic medium consisting of a ammonium cation and complex anion, $(C_{10}H_{21})_3NH^{+1}$ $UO_2(NO_3)^{-1}$, for example. Selectivity of the amines for uranium (VI) is in the order: tertiary > secondary > primary. An anionic extracting system use extensively in laboratories and industry consists of triisooctyl amine (TIOA) in kerosene. Uranium is stripped with sodium sulfate or sodium carbonate solution. A number of mineral and organic acids have been used with the system: hydrochloric, sulfuric, nitric, phosphoric, hydrofluoric, acetic oxalic, formic, and maleic acid. Stripping is accomplished with dilute acid solutions.

Extraction chromatography is a simple and relatively quick method for the separation of uranium on a highly selective, efficient column system. One separation column consist of a triamyl-phosphate $[(C_5H_{11}O)_3PO]$ and diamylamylphosphonate (DAAP) $[C_5H_{11}O)_2(C_5H_{11})PO]$ mixture in an apolar polymeric matrix. In nitric acid, uranyl nitrate forms a complex with DAAP that is soluble in triamylphosphate. Uranium can be separated in this system from many other metal ions, including thorium and the transuranium ions plutonium, americium, and neptunium. It is eluted from the column with the addition of oxalate to the eluent. Another extraction chromatography column uses octylphenyl-N,N-diisobutyl carbamoylphoshpine oxide (CMPO) dissolved in TBP and fixed on the resin matrix for isolation of uranium in nitric acid. Elution occurs with the addition of oxalic acid to the eluent.

ION-EXCHANGE CHROMATOGRAPHY. Both cation- and anion-exchange chromatography have been used to separate uranium from other metal ions. Both stable forms of uranium, uranium (IV and VI) are absorbed on cation-exchange resins. Uranium (IV) is more strongly absorbed, and separation of uranium (VI) (UO_2^{+2}) is limited. On some cation-exchange columns, the ion also tends to tail into other ion fractions during elution. Absorption increases with temperature, however, and increasing the pH also increases absorption up to the beginning of formation of hydrolytic precipitates at pH 3.8. In strong acid solutions, uranium (VI) is weakly absorbed compared to uranium (III and IV) cations. Use of complexing agents increases specificity either by elution of uranium (VI) with common complexes-forming anions such as chloride, fluoride, nitrate, carbonate, and sulfate or by forming EDTA, oxalate, acetate, or sulfate complexes with cations in the analyte, producing a more pronounced difference in absorption of the ions on the exchange resin. A general procedure for separating uranium (VI) from other metals using the first method is to absorb uranium (VI) at pH of 1.5 to 2 and elute the metal with acetate solution.

Anion-exchange chromatography of uranium takes advantage of the stable anionic complexes formed by the various oxidation states of uranium, especially uranium (VI), with many common anions. Uranium (VI) forms both anionic or neutral complexes with acetate, chloride, fluoride, carbonate, nitrate, sulfate, and phosphate. Strong anion-exchange resins are more selective and have a greater capacity than weak exchangers whose use is more limited. Factors that affect the separations include uranium oxidation state and concentration; type of anion and concentration; presence and concentration of other metallic ions and foreign ions; temperature, resin, size, porosity, and cross-linking. The various oxidation states of uranium and other metal ions, particularly the actinides, and the effect of pH on formation of complexes and net charge of the column provide two controllable variable to control the separation process.

A number of chromatographic systems are available for uranium separation on anion-exchange resins. In hydrochloric acid uranium is often absorbed and other cations are not. Uranium (VI) can be absorbed from concentrated hydrochloric acid while alkali metals, alkaline earths, rare earths, aluminum, yttrium, actinium, and thorium are washed off the column. In contrast, uranium, molybdenum, bismuth, tin, technetium, polonium, plutonium and many transition metals are absorbed on the column, and uranium is eluted exclusively with dilute hydrochloric acid. Various oxidation states provide another method of separation. Uranium (IV) is separated from praseodymium (IV), and thorium (IV) with 8 M hydrochloric acid. Thorium, plutonium, zirconium, neptunium, and uranium can be separated individually by absorbing all the ions except thorium from concentrated hydrochloric acid Plutonium (III) elutes with concentrated acid, zirconium at 7.5 M, neptunium (IV) with 6 M hydrochloric acid and 5 percent hydroxylamine hydrochloride, and uranium at 0.1 M acid. Uranium (IV) can be separated from uranium (VI) because both strongly absorb from concentrated hydrochloric acid, but they separate at 6 M acid because uranium (IV) is not absorbed at that concentration. Uranium (VI) absorbs strongly on an anion-exchange resin in dilute hydrofluoric acid, and the absorption decreases with increasing acid concentration. Nitric acid provides an excellent method to purify uranium, because uranium is more strongly absorbed from a nitric acid/nitrate solution. More selectivity is achieved when acid concentration is low and nitrate concentrations high. Absorbance is greatest when aluminum nitrate is use as the source of nitrate. Ethyl alcohol increases absorbance significantly.

ELECTRODEPOSITION. Electrochemical procedures have been used to separate metal ions from uranium in solution by depositing them on a mercury cathode from a sulfuric acid solution, using 5 amps for one hour. Uranium is deposited at a cathode from acetate, carbonate, oxalate, formate, phosphate, fluoride, and chloride solutions to produce a thin, uniform film for alpha and fission counting. This is the primary use of electrodeposition of uranium in analytical work. In another procedure, uranium (VI) is electroplated on a platinum electrode from the basic solution adjacent

to the cathode that exist in a slightly acidic bulk solution. The conditions of the process should be carefully controlled to obtain high yields and adherent coatings on the electrode.

VOLATILIZATION. Several halides of uranium and the uranyl ion are volatile and have the potential for separation by sublimation or fractional distillation. Practically, however, their volatility is not used to separate uranium in analytical procedures because of technical problems or the high temperatures that are required for some procedures, but volatilization has been used in industrial processes. Uranium hexafluoride and uranyl hexafluoride are volatile, and the property is used to separate ^{235}U from ^{238}U in natural uranium isotope mixtures. Uranium tetrachloride and hexachloride are also volatile, and uranium has been isolated from phosphate rock by heating with a mixture of chlorine and carbon monoxide at 800 °C and collecting the tetrachloride.

Methods of Analysis

Macroquantities of uranium, essentially ^{238}U, are determined by fluorimetry. During the separation and purification process, the sample is eventually fused at 625 °C in a flux mixture containing potassium carbonate, sodium carbonate, and sodium fluoride. The residue is exposed to light and its fluorescence is measured. Total uranium or individual radionuclides of uranium, ^{234}U, ^{235}U, and ^{238}U, can be determined from their alpha particle emissions. Uranium radionuclides are collected by evaporating the sample to dryness on a stainless steel planchet, by microprecipitation with a carrier, such as lanthanum or cerium fluoride, or electrodepositon on a platinum disc. Total alpha activity is determined with a gas-flow proportional counter or an alpha liquid scintillation system. Individual radionuclides are measured by alpha spectrometry. Alpha emissions from ^{232}U are used as a tracer to determine chemical recovery.

Compiled from: Allard et al., 1984; Ahrland, 1986; Baes and Mesmer, 1976; Bard, 1985; Booman and Rein, 1962; Choppin et al., 1995; Considine and Considine, 1983; Cotton and Wilkinson, 1988; CRC, 1998-99; DOE, 1990, 1995, and 1997; EPA, 1973; Ehmann and Vance, 1991; Fritz and Weigel, 1995; Greenwood and Earnshaw, 1984; Grindler, 1962; Hampel, 1968; Hassinsky and Adloff, 1965; Katz et al., 1986; Katzin, 1986; SCA, 2001; Weigel, 1986.

14.10.9.12 Zirconium

Zirconium, atomic number 40, is a member of the second-row transition elements. It exhibits oxidation states of +2, +3, and +4, and the +4 state is the most common in both the solid state and in solution. It is immediately above hafnium in the periodic table, and both elements have

very similar chemical properties, more so than any other two elements in the periodic table. It is very difficult, but not impossible, to prepare a sample of zirconium without the presence of hafnium.

Isotopes

There are twenty-nine isotopes of zirconium, including five metastable states, with mass numbers from 81 through 104. Five are naturally occurring, ^{90}Zr, ^{91}Zr, ^{92}Zr, ^{94}Zr, and ^{96}Zr, although the least abundant, ^{96}Zr, is radioactive with an exceptionally long half-life of 3.56×10^{17} y. The remaining isotopes have a half-life of milliseconds to days. The lower mass number isotopes decay primarily by electron capture and the upper mass number isotopes are beta emitters. ^{95}Zr ($t_{1/2}$=64.0 d) and ^{97}Zr ($t_{1/2}$=16.9 h) are fission products and are beta emitters. ^{93}Zr ($t_{1/2}=1.53 \times 10^{6}$y) is a rare fission product, and ^{98}Zr, and ^{99}Zr are short-lived products with half-lives of 30.7 s and 2.1 s, respectively. All are beta emitters.

Occurrence and Uses

Zirconium is one of the most abundant and widely distributed metals found in the earth's crust. It is so reactive that it is found only in the combined state, principally in two minerals, zircon, zircon orthosilicate ($ZrSiO_4$), and baddeleyite, mostly zirconium dioxide (ZrO_2). Zirkite is a commercial ore that consists of both minerals. Hafnium is a minor constituent of all zirconium minerals.

In the production of zirconium metal, zirconium sands, primarily zirconium dioxide, is passed through an electrostatic separator to remove titanium minerals, a magnetic separator to remove iron, ileminite, and garnet, and a gravity separator to remove the less dense silica. The recovered zircon is heated with carbon in an arc furnace to form zirconium cyanonitride, an interstitial solution of carbon, nitrogen, and oxygen (mostly carbon) in the metal. Silicon evaporates as silicon monoxide (SiO), becoming silicon dioxide (SiO_2) at the mouth of the furnace. The hot zirconium cyanonitride is treated with chlorine forming volatile zirconium tetrachloride ($ZrCl_4$), which is purified by sublimation to remove, among other impurities, contaminating oxides. The chloride is reduced in the Kroll process, in turn, with liquid magnesium under conditions that produce a metal sponge. The byproduct, magnesium chloride ($MgCl_2$), is then removed by melting the chloride, draining it off, and removing its residues by vacuum distillation. The zirconium sponge is crushed, melted into bars, arc-melted in an inert atmosphere, and formed into ingots. For additional purification, the van Arkel-de Boer process removes all nitrogen and oxygen. Crude zirconium is heated to 200 °C in an evacuated container containing a small amount of iodine to form volatile zirconium tetraiodide (ZrI_4). A tungsten filament is electrically

heated to 1,300 °C, decomposing the iodide and depositing zirconium on the filament. The commercial grade of zirconium still contains up to three percent hafnium. To be used in nuclear reactors, however, hafnium should be removed. Separation is usually accomplished by solvent extraction of zirconium from an aqueous solution of zirconium tetrachloride as a complex ion (phosphine oxide, for example), by ion-exchange, fractional crystallization of complex fluoride salts, distillation of complexes of zirconium tetrachloride with phosphorus pentachloride or phosphorus oxychloride, or differential reduction of the mixed tetrachlorides (zirconium tetrachloride is more easily reduced to the nonvolatile trichloride than hafnium tetrachloride.

^{95}Zr and ^{97}Zr are fission products and are also produced by bombardment of naturally occurring ^{94}Zr and ^{96}Zr, respectively, with thermal neutrons. Stable ^{90}Zr is a product of the ^{90}Sr decay chain:

$$^{90}_{38}\mathrm{Sr} \rightarrow {}^{90}_{39}\mathrm{Y} + \beta \rightarrow {}^{90}_{40}\mathrm{Zr} + \beta + \gamma$$

Zirconium metal and its alloys are highly corrosion resistant and withstands streams of heated water under high pressure. These properties, along with their low cross section for thermal neutrons, make them an important material for cladding uranium fuel elements and as core armor material in nuclear reactors. It is also used for making corrosive resistant chemical equipment and surgical instruments and making superconducting magnets. Zirconium compounds are also used in the ceramics industry as refractories, glazes, and enamels, in cores for foundry molds, abrasive grits, and components of electrical ceramics. Crystals of zircon are cut and polished to use in jewelry as simulated diamonds. They are also used in pyrotechnics, lamp filaments, in arc lamps, cross-linking agents for polymers, components of catalysts, as bonding agents between metal and ceramics and between ceramics and ceramics, as tanning agents, ion exchangers, and in pharmaceutical agents as deodorants and antidotes for poison ivy. ^{95}Zr is used to follow homogenization of oil products.

Solubility of Compounds

The solution properties of zirconium in water are very complex, mainly because of the formation of colloids and the extensive hydrolysis and polymerization of the zirconium ion. hydrolysis and polymerization are strongly dependent on the pH of the solution, concentration of the ion, and temperature. The nitrate, chloride, bromide, iodide, perchlorate, and sulfate of zirconium are soluble in acid solution, however.

Review of Properties

Pure zirconium is a grey-white (silvery) lustrous metal with a density of 6.49 g/cm^3. It exist in two allotropic forms, alpha and beta, with a transition temperature of 870 °C. The alpha form is stabilized by the common impurity oxygen. The amorphous powder is blue-black. Trace amounts of common impurities (≤ 1 percent), such as oxygen, nitrogen, and carbon, make the metal brittle and difficult to fabricate. The metal is not considered to be a good conductor of heat and electricity, but compared to other metals it is soft, malleable, and ductile. Zirconium forms alloys with most metals except, mercury, the alkali metals, and the alkaline earths. It can absorb up to ten percent oxygen and nitrogen. Zirconium is a superconductor at temperatures near absolute zero, but its superconducting properties improve when the metal is alloyed with niobium and zinc.

Finely divided, dry zirconium (powder and chips) is pyrophoric and extremely hazardous. It is hard to handle and store and should be moistened for safe use. Note, however, that both wetted sponge and wet and dry stored scrap have been reported to spontaneously explode. Caution should also be observed with waste chips produced from machining and cleaning (new) zirconium surfaces. Both can be pyrophoric. In contrast, zirconium in the bulk form is extremely resistant to corrosion at room temperature and remains bright and shiny in air. Resistance is rendered by the formation of a dense, adherent, self-sealing oxide coating. The metal in this form is resistant to acids, alkalis, and seawater. Without the coating, zirconium dissolves in warm hydrochloric and sulfuric acids slowly; dissolution is more rapid in the presence of fluoride ions. The metal is also resistant to high-pressure water streams and high-temperature steam. It also has a low cross-section to thermal neutrons and is resistant to damage from neutron radiation. These properties give pure zirconium (without hafnium) very useful as a fabrication material for nuclear reactors. Zirconium metal alone, however, is not sufficiently resistant to hot water and steam to meet the needs for use in a nuclear reactor. Alloyed with small percentages of tin, iron, nickel, or chromium (Zircalloy), however, the metal meets the standards.

The coated metal is becomes reactive when heated at high temperature (≥ 500 °C) with nonmetals, including hydrogen, oxygen, nitrogen, carbon, and the halogens, and forms solid solutions or compounds with many metals. It reacts slowly with hot concentrated sulfuric and hydrochloric acids, boiling phosphoric acid, and aqua regia. It is also attacked by fused potassium nitrate and potassium hydroxide, but is nonreactive with aqueous alkali solutions. It is not reactive with nitric acid. Hydrofluoric acid is the only reagent that reacts vigorously with zirconium.

Zirconium and its compounds are considered to have a low order of toxicity. Most handling and testing indicate no level of toxicity, but some individual seem to be allergic to zirconium compounds. Inhalation of zirconium compound sprays and metallic zirconium dust have produced inflammatory affects.

Very small quantities of ^{95}Zr have been released to the environment from fuel reprocessing facilities, atmospheric testing, and the Chernobyl accident. With a half-life of 64 days, the contamination of the environment is not significant. Zirconium lost from a waste repository would be expected to move very slowly because of radiocolloidal attraction to surrounding soil particles. Hydrolysis and polymerization renders most zirconium insoluble in natural water, but absorption to suspended particles is expected to provide some mobility in an aqueous environment.

Solution Chemistry

The only important oxidation state of zirconium ions in aqueous solution is +4, making it a essentially a monovalent element. The solution chemistry of zirconium is quite complex, nevertheless, because of the easy formation of colloids and extensive hydrolysis and polymerization reactions that are strongly dependent on pH and ion concentration.

COMPLEXATION. Zirconium ions forms complexes with numerous substances: fluoride, carbonate, borate, oxalate, and other dicarboxylic acids, among others. As a large, highly charged, spherical ion, it exhibits high coordination numbers. One of the important chemical properties of zirconium ions in solution is their formation of a very stable hexafluorozirconate complex, ZrF_6^{-2}. For that reason, hydrofluoric acid (HF) is an excellent solvent for the metal and insoluble zirconium compounds. Unfortunately, the fluorocomplex interferes with most separation and determination steps, and zirconium should be expelled by fuming with sulfuric or perchloric acid before proceeding. The addition of several milliliters of concentrated HF to a cool solution of zirconium carrier and sample will produce initial equilibration; essentially all the zirconium is present in the +4 oxidation state as a fluoride complex. Note that addition of HF to solutions above the azeotropic boiling point of the acid (120 °C) serves no useful purpose and simply evaporates the HF.

Tartrate and citrate ions form stable complexes even in alkaline solutions, and zirconium hydroxide will not precipitate in their presence (see hydrolysis below). Oxalate forms a complex that is less stable. The ion, $[Zr(C_2O_4)_3]^{-2}$, is only stable in acid solution. On addition of base, the complex is destroyed, and zirconium hydroxide precipitates. Sulfuric acid complexes in strongly acidic solutions, forming $Zr(SO_4)_4^{-2}$. In concentrated HCl solutions, $ZrCl_6^{-2}$ is present.

Zirconium ions form chelate complexes with many organic compounds, usually through oxygen atoms in the compounds. Typical examples are: acetylacetone (acac), EDTA, thenoyltrifluoro-acetone (TTA), salicylic acid, mandelic acid, cupferron, and 8-hydroxyquinoline.

HYDROLYSIS. Although Zr^{+4} has a large radius and any +4 cation is extensively hydrolyzed, Zr^{+4} appears to exist at low ion concentrations (approximately 10^{-4} M) and high pH (1-2 M). As the Zr^{+4} concentration increases and the concentration of H^{+1} decreases, however, hydrolysis and polymerization occurs, and one or more polymeric species is dominate in solution. Amorphous hydrous oxides are precipitated near pH 2; they are soluble in base. Because of hydrolysis, soluble salts (nitrate, sulfate, perchlorate, acetate, and halides) form acidic solutions when they dissolve. The reaction seems to be essentially a direct conversion to the tetranuclear $Zr_4(OH)_8(H_2O)_{16}^{+2}$ ion; there is no convincing evidence for the existence of ZrO^{+2}, thought at one time to be present in equilibrium with numerous other hydrolysis products. It should be noted, however, that freshly prepared solutions of zirconium salts might react differently from a solution left standing for several days. Whatever the actual species in solution at any given time, the behavior of zirconium (IV) depends on the pH of the solution, temperature, anion present, and age of solution. In addition, zirconium compounds formed by precipitation from solution usually do not have a constant composition because of their ease of hydrolysis. Even under exacting conditions, it is difficult to obtain zirconium compounds of known, theoretical composition, and on aging, hydrolysis products becomes more polymeric and polydisperse.

In acidic solutions, trace amounts of zirconium are strongly coprecipitated with most precipitates in the absence of complexing ions, especially F^{-1} and $C_2O_4^{-2}$ that form soluble complex ions.

In alkaline solutions, produced by the addition of hydroxide ions or ammonia, a white gelatinous precipitate of zirconium hydroxide forms. Since the hydroxide is not amphoteric, it does not dissolve in excess base. The precipitate is not a true hydroxide but a hydrated oxide, $ZrO_2 \cdot nH_2O$ where *n* represents the variable nature of the water content. Freshly prepared zirconium hydroxide is soluble in acid; but as it dries, its solubility decreases. Precipitation is inhibited by tartrate or citrate ions because Zr^{+4} forms complexes with these organic anions even in alkaline solutions (see "Complexation," above).

In preparing zirconium solutions, it is wise to acidify the solution with the corresponding acid to reduce hydrolysis and avoid precipitation of basic salts. During solubilization and radiochemical equilibrium with a carrier, the tendency of zirconium ions to hydrolyze and polymerize even at low pH should be kept in mind. Often, the formation of a strong complex with fluoride or TTA is necessary.

RADIOCOLLOIDS. Radiocolloids of zirconium are adsorbed on practically any foreign matter (e.g., dirt, glass, etc.). Their formation can cause problems with dissolution, achieving radiochemical equilibrium, and analysis. Generally, it is necessary to form a strong complex with fluoride (see caution above) or TTA.

Dissolution of Samples

Metallic zirconium is dissolved in hydrofluoric acid, hot aqua regia, or hot concentrated sulfuric acid. Hydrofluoric acid should be removed by fuming with sulfuric acid or perchloric acid (caution), because fluoride interferes with most separation and analytical procedures. Zirconium ores, rocks, and minerals are fused at high temperatures with sodium carbonate, potassium thiosulfate, sodium peroxide, sodium tetraborate, or potassium hydrogen fluoride (remove fluoride). The residue is dissolved in dilute acid or water and might require filtration to collect a residue of zirconia (impure ZrO_2), which is dissolved in acid. As a minor constituent of natural sample or as a result of formation by nuclear reactions, zirconium typically dissolves during dissolution of the major constituents. The tendency to polymerize under low concentrations of acid and the formation of insoluble zirconium phosphates should be considered in any dissolution process. The tendency of zirconium to polymerize and form radiocolloids makes it important to insure equilibrium with any carrier added. Generally, formation of strong complexes with fluoride or TTA is necessary.

Separation Methods

PRECIPITATION AND COPRECIPITATION. One of the most insoluble precipitating agents is ammonium hydrogen phosphate $(NH_4)_2HPO_4$) in 20 percent sulfuric acid. It has the advantage that it can be dissolved by hydrofluoric acid, forming hexafluorozirconate. This complex ion also forms insoluble barium hexafluorozirconate ($BaZrF_6$), a precipitating agent that allows the precipitation of zirconium in the presence of niobium that is soluble as the heptafluoroniobate (NbF_7^{-2}). Other precipitating agents include the iodate (from 8 M nitric acid), cupferrate, the hydroxide, peroxide, selenate, and mandelate. Cupferron is used in sulfuric or hydrochloric acid solutions. It is one of the few precipitating agents in which fluoride does not interfere, but iron and titanium, among other cations, are also precipitated. The precipitate can be heated in a furnace at 800 °C to produce zirconium dioxide for the gravimetric determination of zirconium. The hydroxide begins to precipitate at pH 2 and is complete at pH 4, depending on the presence of zirconium complexes. It is not recommended unless other cations are absent, because it absorbs or coprecipitates almost all other ions. Peroxide is formed from a solution of hydrogen peroxide in acid. Selenious acid in dilute hydrochloric acid separates zirconium from some of the transition elements and thorium. Mandelic acid in hot dilute hydrochloric acid quantitatively and

specifically precipitates zirconium (and hafnium) ions. Large amounts of titanium, tin, iron, and other ions might be partially coprecipitated, but they can be eliminated by reprecipitation.

Trace quantities of zirconium can be strongly coprecipitated by most precipitates from strong acid solutions that do not contain complex-forming ions. Bismuth and ceric phosphate readily carries zirconium, and in the absence of holdback carriers, it is almost quantitatively carried by rare-earth fluorides. Ferric hydroxide and thorium iodate are also effective carriers.

SOLVENT EXTRACTION. Several extractants have been used to selectively remove zirconium from aqueous solutions; most are organophosphorus compounds. Di-*n*-butylphosphoric acid (DBPA) (di-*n*-butylphosphate) is an extractant for zirconium and niobium. It is effective in extracting tracer and macro quantities of zirconium from 1 M aqueous solutions of nitric, hydrochloric, perchloric, and sulfuric acids and in separating it from many other elements. A 0.06 M solution in di-*n*-butylether containing three percent hydrogen peroxide extracts more than 95 percent zirconium but less than one percent niobium. Tin and indium were also extracted by this mixture. Tri-*n*-butylphosphate (TBP) is an excellent solvent for zirconium. It is used pure or with several nonpolar diluents, ethers, kerosene, or carbon tetrachloride. Extractability increases with acid strength. A 0.01 M solution of tri-*n*-octylphosphine oxide (TOPO) in cyclohexane has been use to separate zirconium form iron, molybdenum, vanadium, thorium, and hafnium.

TTA and hexone (methyl isobutyl ketone) are two nonphosphorus extractants employed for separating zirconium. TTA is highly selective. A 0.5 M solution in xylene separates zirconium from aluminum, iron, thorium, uranium, and rare earths in a 6 M hydrochloric acid solution. At tracers levels, the reagent can separate ^{95}Zr from all other fission products. It is also used to separate zirconium from hafnium. In the analysis of zirconium in zirconium-niobium-tantalum alloys, hexone separates zirconium from an aqueous solution that is 10 M hydrochloric acid and 6 M sulfuric acid. This is one of the few methods that can be use to separate zirconium from these metals.

ION-EXCHANGE CHROMATOGRAPHY. Zirconium can be separated form many other cations by both cation- and anion-exchange chromatography. The technique represents the best laboratory method for separating zirconium and hafnium. Cation-exchange columns strongly absorb zirconium ions, but macro quantities of zirconium and hafnium can be purified as aqueous colloidal solutions of their hydrous oxides on an organic cation-exchange resin. Many cations are retained on the column, but zirconium and hafnium, under these conditions, are not. The recovery can be as high as 99 percent with successive passages, but titanium and iron are not removed. Zirconium and hafnium can be separated on a sulfuric-acid column from 2 M perchloric acid. Hafnium is eluted first with 6 M hydrochloric acid. Fluoride complexes of

zirconium and hafnium can be separated from other non-complexing cations, because the negative complex ions are not absorb and the non-complexing ions are retained. Zirconium, hafnium, and niobium are eluted from rare earths and alkaline earths on cation-exchange columns with citrate. The three elements can be then be separated by the selection of appropriate citrate buffers, but the separations are not quantitative.

The formation of stable zirconium complexes is the basis of anion-exchange chromatography of the metal. Separation of zirconium and hafnium from each other and form other cations can be achieved in hydrochloric-hydrofluoric acid mixtures. Separation of zirconium from hafnium, niobium, protactinium, and thorium, respectively, is accomplished by selection of the proper eluting agent. Elution of hafnium first with 9 M hydrochloric acid separates zirconium from hafnium, for example, while elution with 0.2 M hydrochloric acid/0.01M hydrofluoric acid recovers zirconium first. Elution with 6-7 M hydrochloric acid separates zirconium from niobium, in another example.

Methods of Analysis

^{95}Zr decays with a half-life of 65.5 d, emitting a beta particle accompanied by gamma-ray emission. After several half-lives, it is in transient equilibrium with its progeny, ^{95}Nb, which has a half-life of 35.0 d and is also a beta and gamma emitter. The progeny of ^{95}Nb is stable ^{95}Mo. Fresh samples of ^{95}Zr are analyzed by their gamma-ray emission. Zirconium is collected by precipitation and filtration. The sample and filter are heated at 800 °C for one hour to decompose the filter and convert zirconium to its oxide. Zirconium dioxide (ZrO_2) is collected by filtration, dried, and counted immediately.

Compiled from: Baes and Mesmer, 1976; Choppin et al., 1995; Considine and Considine, 1983; Cotton and Wilkinson, 1988; CRC, 1998-99; Ehmann and Vance, 1991; EPA, 1973; Greenwood and Earnshaw, 1984; Hahn, 1961; Hassinsky and Adloff, 1965; Latimer, 1952; Steinberg, 1960.

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15 NUCLEAR COUNTING INSTRUMENTATION

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15.1 Introduction

This chapter presents descriptions of counting techniques to help the user to determine what radioanalytical measurement method(s) best suit a given need. References cited in the text provide additional details of how these measurements are made. The primary focus here is on the variables that ultimately affect the bias and precision of the counting data. The type of information that is desired—in relation to the type of radiation to detect—will determine the type of instrument and associated technique one will use to generate data. For example, samples containing a single radionuclide of high purity, sufficient energy, and ample activity may only require a simple detector system. In this case, the associated investigation techniques may offer no complications other than those related to calibration and reproducibility. At the other extreme, a sample or set of samples may require quantitative identification of many radionuclides or the laboratory may need to prepare unique calibration standards. In the latter case, specialized instruments are available. Typically, a radiochemical laboratory will encounter samples routinely that require a level of information between the two extremes described above.

A typical laboratory may be equipped with the following nuclear counting instrumentation:

- Proportional or Geiger-Mueller detectors for alpha and beta counting;
- Sodium iodide or high resolution germanium detectors for gamma detection and spectrometry;
- Solid state detectors for alpha spectrometry;
- Scintillation counters suitable for both alpha- or beta-emitting radionuclides; and
- Multichannel analyzers for alpha and gamma-ray spectrometry.

A basic requirement for accurate measurements is the use of high quality standards, traceable to a national standards organization (Section 15.9; ANSI N42.22, ANSI N42.23), to calibrate

instrumentation. Generally, with the present availability of good standards, radiochemistry laboratories rarely require instrumentation suitable for producing their own calibration standards. However, it is always advisable to compare each new standard received against the previous standard. The next three main sections of the chapter describe counting instrumentation for alpha (Section 15.2), beta (Section 15.3), and gamma (Section 15.4) radiation. In a number of cases the same instrumentation is used for radionuclides with one or more types of radiation. Note that a review covering descriptions of radionuclides, types of radiation, associated principles, and definitions for related terminology is given in Appendix A of this manual. The discussion next turns to several specific areas to cover spectrometry (Section 15.5), special instrumentation (Section 15.6), and spectrometers and energy-dependent detectors (Section 15.7). Shielding (Section 15.8) to reduce detector background of nuclear counting instruments and instrument calibration (Section 15.9) follows. This chapter closes with a discussion of other nuclear counting instrumentation considerations (Section 15.10) including a discussion on non-nuclear instrumentation (Section 15.10.4).

15.2 Alpha Counting

15.2.1 Introduction

Alpha particles are relatively massive, expend their energy over short distances, and typically exhibit limited penetration into neighboring materials. Alpha particles are also characterized by an intense loss of energy while passing through matter (see ICRU, 1992, for a discussion of dose equivalents and linear energy transfer). This loss of energy is used to differentiate alpha radioactivity from other types through the dense ionization or intense scintillation it produces. This high rate of loss of energy in passing through matter, however, also makes sample preparation conditions for alpha counting more stringent than is necessary for other types of radiation. An example of direct alpha counting to determine total alpha activity is given in ASTM C799.

Alpha radioactivity normally is measured by one of several types of detectors in combination with suitable electronic components. The detector devices most used are ionization chambers, proportional counters, silicon semiconductor detectors, and scintillation counters. The associated electronic components in all cases include high-voltage power supplies, preamplifiers, amplifiers, scalers, analog-to-digital converters, and recording devices.

The measured alpha-counting rate from a sample will depend on a number of variables. The most important of these variables are:

- Geometry;
- Source diameter;
- Self-absorption;
- Absorption in air and detector window;
- Coincidence losses; and
- Backscatter.

These are discussed in detail in the literature (Blanchard et al., 1960; Hallden and Fisenne, 1963), and can be measured or corrected for in many cases by holding conditions constant during the counting of samples and standards.

Alpha counters have low backgrounds and high efficiencies. Thus, outside sources of alpha radiation will not impact the counting process and the instrument essentially focuses on the alpha source presented by the sample. However, some counters are easily contaminated internally and care should be taken to avoid contamination. Silicon detectors operated in a vacuum may become contaminated due to recoil from sources (Merritt et al., 1956). Some alpha counters are sensitive to beta radiation depending on the detector (Blanchard et al., 1960; Hallden and Fisenne, 1963). In these cases, electronic discrimination is often used to eliminate the smaller pulses due to beta particles. A discussion of alpha particle attenuation can be found in Section 15.10.1.1.

15.2.2 Detectors for Alpha Counting

15.2.2.1 Ionization Chambers

As the incident particle enters the ionization chamber, ionization occurs through the interaction of the particle with the fill gas. The secondary electrons produced through these interactions are accelerated toward the anode as a result of the bias applied to the system. An ion current is produced at the anode as a result of the collection of the free electrons (negative ions) generated through ionization interactions. The charge collected at the anode is collected across an RC circuit resulting in a change in potential across a capacitor. The change in potential is thus related to the charge produced from the collection of electrons produced through the ionization interactions of the incident particle.

15.2.2.2 Proportional Counters

As the incident particle enters the proportional counter, ionization occurs through the interaction of the particle with the fill gas. The secondary electrons produced through these interactions are accelerated toward the anode as a result of the bias applied to the system. In proportional

counters, the free electrons gain sufficient kinetic energy during acceleration to produce secondary ionization as they migrate toward the anode. This effect, known as "gas multiplication," is used to amplify the charge collected at the anode. Similar to ionization chambers, the charge collected at the anode is collected across an RC circuit resulting in a change in potential across a capacitor. As a result of gas multiplication, the voltage pulse produced is considerably larger than the pulse produced in an ionization chamber. The magnitude of the voltage pulse is thus proportional to the original number of ion pairs formed by the incident particle.

Proportional detectors are generally constructed of stainless steel, oxygen free/high conductivity (OFHC) copper, or aluminum. No additional shielding is required for alpha proportional counting. The counter should be capable of accepting mounts up to 51 mm in diameter. Proportional counters are available in two types, either with or without a window between the sample and the counting chamber. The manufacturer's specifications for either type should include performance estimates of background count rate, length and slope of the voltage plateau, and efficiency of counting a specified electrodeposited standard source, along with the type of gas used in the tests. For a window flow counter, the window thickness—in milligrams per square centimeter—also should be specified. With a windowless flow counter the sample and sample mount should be made of an electrical conductor in order to avoid erratic behavior due to static charge buildup.

Typical parameters for the alpha windowless flow counter are:

background count rate	=	10 counts/h or 2.8×10^{-3} cps
length of voltage plateau	=	300 V
slope of voltage plateau	=	1%/100 V for an electrodeposited source

For a window flow counter, typical values are:

window thickness	=	0.08 to 0.5 mg/cm^2
background count rate	=	10 counts/h or 2.8×10^{-3} cps
length of voltage plateau	=	300 V
slope of voltage plateau	=	1%/100 V for an electrodeposited source
efficiency	=	35 to 40 percent for an electrodeposited source

15.2.2.3 Scintillation Counters

In a scintillation counter, the alpha particle transfers energy to a scintillator, such as zinc sulfide (silver activated). The transfer of energy to the scintillator results in the production of light at a

wavelength characteristic to the scintillator, and with an intensity proportional to the energy transmitted from the alpha particle. The scintillator medium is placed in close proximity to the cathode of a multiplier phototube; light photons from the scintillator strike the photo cathode, and electrons are emitted. The photoelectrons are passed through a series of dynodes resulting in the multiplication of electrons at each stage of the multiplier phototube. After amplification, a typical scintillation vent will give rise to 10^7 to 10^{10} electrons, which is sufficient to serve as a signal charge for the scintillation event. The elèctrons are collected across an RC circuit, which results in a change in potential across a capacitor, thus giving rise to a pulse used as the electronic signal of the initial scintillation event.

The counter size is limited by the multiplier phototube size, a diameter of 51 mm being the most common. Two types of systems may be employed. In the first, the phosphor is optically coupled to the multiplier phototube and either is covered with a thin (<1 mg/cm^2) opaque window or enclosed in a light-proof sample changer. With the sample placed as close as possible to the scintillator, efficiencies approaching 40 percent may be obtained. The second system employs a bare multiplier phototube housed in a light-proof assembly. The sample is mounted in contact with a disposable zinc sulfide disk and placed on the phototube for counting. This system gives efficiencies approaching 50 percent, is associated with a slightly lower background, and less chance of counter contamination.

A major advantage of alpha scintillation counting is that the sample need not be conducting. For a 51 mm multiplier phototube with the phosphor coupled to the tube, typical values obtained are a background count rate of 0.006 cps and an efficiency for an electrodeposited standard source of 35 to 40 percent. With a disposable phosphor mounted on the sample, typical values are a background count rate of 0.003 cps and an efficiency for an electrodeposited standard source of 45 to 50 percent. For both systems, voltage plateau length is 150 V with a slope of 5 percent/100 V.

15.2.2.4 Liquid Scintillation Counters

Liquid scintillation counting of alpha emitters with a commercially available instrument overcomes many of the problems inherent in other techniques (Passo and Cook 1994; Horrocks, 1974; DeFilippis, 1990; Friedlander et al., 1964; Curtis et al., 1955; Matt and Ramsden, 1964; Overman and Clark, 1960; Price, 1964; Flynn et al., 1971). Typical background counting rates range from 0.1 to 0.2 cps. Sample preparation, after radiochemical separation is performed, involves mixing the sample aliquant with a suitable liquid scintillator solution or gel phosphor before counting. In this way, planchet preparation is eliminated, volatile components are retained, and the completely enclosed sample cannot contaminate the counting chamber. Ideally, the

sample is uniformly distributed in the scintillator so there is no self-absorption. This results in a counting efficiency of almost 100 percent. Because of the high alpha energies, considerable chemical quenching effects can be tolerated before counting efficiency is reduced. Coincidence losses are small in liquid scintillation counting at count rates up to 2×10^4 cps. For samples that contain both alpha and high-energy beta emitters, difficulties do arise in distinguishing between the two. The problem is due primarily to the broad continuum of beta energy distribution up to the maximum energy and the poor resolution of liquid scintillation spectrometers. This problem is aggravated because the light yield per million electron volts of alpha particles in most liquid scintillators is approximately tenfold lower than a beta particle of equivalent energy, putting the pulses from alphas and high-energy betas in the same region. Correction for beta activity may be made by certain mathematical, graphical or electronic techniques (see discussion of pulse shape discrimination in Section 15.5.4). It is preferable to separate the alpha emitter from the bulk of the beta activity by chemistry.

15.2.2.5 Semiconductor Detectors

Semiconductor detectors used for alpha counting are essentially solid-state ionization chambers. The ionization of the gas in an ionization chamber by alpha particles produces electron-ion pairs, while in a semiconductor detector electron-hole pairs are produced. The liberated charge is collected by an electric field and amplified by a charge-sensitive amplifier. In general, ion-implanted-silicon or silicon surface barrier detectors are used for alpha counting. These detectors are n-type base material upon which gold is evaporated to make a contact. The semiconductor material must have a high resistivity since the background is a function of the leakage current. This leakage current is present in an electric field since the starting material is a semiconductor, not an insulator. The leakage current of silicon diodes doubles for every 5.5 to 7.5 °C change in ambient temperature. Since the preamp HV bias resistor is a noise contributor, it is necessarily of high value, typically 100 megohm. With a surface barrier detector having leakage current of 0.5 μA, the change in bias voltage at the detector for a 2 °C change in ambient temperature can be as much as 13V. This is enough bias change to affect overall gain of the detector-preamplifier by a substantial amount. The reversed bias that is applied reduces the leakage current and a depletion layer of free-charge carriers is created. This layer is very thin and the leakage current is extremely low; therefore, the interactions of photons with the detector will have negligible effect. Since the detector shows a linear response with energy, any interactions of beta particles with the detector can be eliminated by electronic discrimination. The semiconductor is of special interest in alpha counting where spectrometric measurements may be made since the average energy required to produce an electron-hole pair in silicon is 3.5±0.1 eV compared to the 25 to 30 eV needed to produce an ion pair in a gridded ionization chamber. Consequently, silicon detectors provide much improved resolution and also normally have lower background count rates.

The detector size is generally less than 25 mm in diameter since the resolution decreases and cost increases with detector size. For best results, the sample should be electrodeposited to make a lower mass source (Puphal and Olson, 1972). However, micro precipitation as fluorides has been reported with only slight lose of resolution (Sill and Williams, 1981; Hindman, 1983). The detector is operated in a vacuum chamber. Typical backgrounds range from 8×10^{-5} to 2×10^{-4} cps.

15.3 Beta Counting

15.3.1 Introduction

This section covers the general techniques used to measure the beta particle activity resulting from radiochemical separations of specific nuclides or groups of nuclides. Beta radioactivity may be measured by several types of instruments that provide a detector and a combined amplifier, power supply, and scaler. The most widely used detectors are proportional or Geiger-Mueller counters—however, scintillation systems offer certain advantages (see discussion in Section 15.3.3). An example of the measurement of fission product activity by beta counting is given in ASTM C799, D1890, and D3648.

15.3.2 Proportional Counter

Among the gas ionization-type detectors, the proportional type counter is preferable because of the shorter resolving time and greater stability of the instrument. For preparing solid sources for beta activity measurement, the sample is reduced to the minimum weight of solid material having measurable beta activity by dissolution, radiochemistry, precipitation, or ion exchange techniques. For measuring solid sources resulting from individual radiochemical separation procedures, the precipitate is appropriately mounted for counting.

Beta particles entering the sensitive region of the detector produce ionization that is converted into an electrical pulse suitable for counting. The number of pulses per unit time is directly related to the disintegration rate of the sample by an overall efficiency factor. This factor combines the effects of sample-to-detector geometry, sample self-shielding, backscatter, absorption in air and in the detector window (if any), and detector efficiency. Because most of these individual components in the overall beta-particle detection efficiency factor vary with beta energy, the situation can become complex when a mixture of beta emitters is present in the sample. The overall detection efficiency factor may be empirically determined with prepared standards of composition identical to those of the sample specimen, or an arbitrary efficiency factor can be defined in terms of a single standard such as cesium-137 (^{137}Cs) or other nuclide.

Gross counts can provide only a very limited amount of information and therefore should be used only for screening purposes or to indicate trends.

15.3.3 Liquid Scintillation

Liquid scintillation counting (LSC) avoids many sources of error associated with counting solid beta sources, such as self-absorption, back scattering, loss of activity during evaporation due to volatilization or spattering, and variable detection efficiency over a wide beta-energy range. In addition to the greatly improved accuracy offered by liquid scintillation counting, sample preparation time and counting times are significantly shorter. Sample preparation involves only adding a sample aliquant to the scintillator or gel phosphor. Because every radioactive atom is essentially surrounded by detector molecules, the probability of detection is quite high even for low-energy beta particles. Radionuclides having maximum beta energies of 200 keV or more are detected with essentially 100 percent efficiency. Liquid scintillation can, at times, be disadvantageous due to chemiluminescence, phosphorescence, quenching, or the typically higher backgrounds.

The observed count rate for a liquid scintillation sample is directly related to the beta (plus conversion electron) and positron emission rate in most cases. The important exceptions are: beta emitters whose maximum energy is below 200 keV, and counting systems wherein quenching decreases the expected photon yield, thereby decreasing the overall detection efficiency significantly below 100 percent. Low-energy beta emitters, such as tritium (^{3}H) or carbon-14 (^{14}C), can be measured accurately only when the appropriate detection efficiency factor has been determined with a known amount of the same radionuclide counted under identical conditions. Quenching losses are greatest at low beta energies. Quenching may be evaluated by comparison to known quench standards of the same radionuclide, using the channel ratio technique, or with other techniques as described in the manufacturer's instructions.

For measurements in which data are expressed relative to a defined standard, the individual correction factors cancel whenever sample composition, sample weight, and counting configuration and geometry remain constant during the standardization and tests.

Liquid scintillation counting systems use an organic phosphor as the primary detector. This organic phosphor is combined with the sample in an appropriate solvent that achieves a uniform dispersion. A second organic phosphor often is included in the liquid scintillation cocktail as a wavelength shifter. The wave length shifter efficiently absorbs the photons of the primary phosphor and re-emits them at a longer wavelength more compatible with the multiplier phototube. Liquid scintillation counting systems use either a single multiplier phototube or two

multiplier phototubes in coincidence. The coincidence counting arrangement is less likely to accept a spurious noise pulse that occurs in a single phototube, and thus provides lower background. The requirement that both multiplier phototubes respond to each has a slight effect on the overall detection efficiency of betas with E-max >200 keV; however, system response to beta E-max <200 keV will be significant. The need to minimize detectable radioactivity in the detector and its surroundings is likewise important in liquid scintillation counting. To achieve this, scintillation-grade organic phosphors and solvents are prepared from low ^{14}C materials such as petroleum. The counting vials are of low potassium glass or plastic to minimize counts due to potassium-40 (^{40}K). Liquid scintillation provides a fixed geometry from a given size counting vial and liquid volume. The calibration of liquid scintillation counting detectors is given in ASTM E181. The use of an organic phosphor for liquid scintillation counting creates a mixed waste. Chapter 20 of this manual addresses the proper disposal of these materials.

Another approach to LSC without the use of organic phosphors is Cerenkov counting. When charged particles pass through a dielectric medium, such as water, and there is an exchange of energy to the molecules of that medium, Cerenkov radiation is produced. This happens if the charged particles are moving faster than the speed of light and the exchange of energy produces electronic polarization, then when the polarized molecules return to a normal state the excess energy is released as electromagnetic radiation (Kessler, 1986). Wave shifters are usually employed to convert the ultraviolet Cerenkov radiation to the visible range. Although Cerenkov counting efficiencies are about 20 to 50 percent (Scarpitta and Fisenne, 1996) lower than when organic phosphors are used, mixed waste disposal is eliminated.

15.3.4 Solid Organic Scintillators

Organic scintillators, such as p-terphenyl plus a wave shifter in a plastic monomer, are polymerized to form sheet material of any desired thickness. The plastic phosphor counting system (Campion et al., 1960) has its widest use as a beta particle detector for separated, solid samples rather than for beta spectrometry applications.

The plastic beta scintillator phosphor is mounted directly on the sample and is discarded after counting. The phosphor-sample sandwich is placed in direct contact with the multiplier phototube yielding essentially a 2-π configuration. Since the output pulse of the detector system is energy dependent, the counting efficiency for a given phosphor thickness of 0.25 mm yields the highest counting efficiency with the lowest background.

Solid samples (precipitates from radiochemical separations) containing 3 to 5 mg/cm^2 of stable carrier are measured in such a system. For yttrium-90 (^{90}Y) a solid sample of this type would have a counting efficiency of 45 to 50 percent.

A plastic scintillator/phosphor system with a 25 mm multiplier phototube shielded with 12.7 mm of lead has background in the order of 4×10^{-2} cps. For very low backgrounds, about 4×10^{-3} cps, the multiplier phototube and sample assembly are fitted into a well-type hollow anode Geiger tube operated in anti-coincidence. The entire assembly is then placed in a heavy shield.

The system has many advantages but reduction of background is probably most important. The reduction occurs since the scintillator does not see the surrounding mechanical components of the counter. The additional advantage of keeping the counter itself free from contamination by enclosing the phosphor-sample sandwich is also important.

A note of caution is advisable at this point. Any beta particle detection system, whether internal gas counters or scintillation counters, will detect alpha particles. It is not possible to electronically discriminate against all the alpha pulses.

If a sample is suspected of containing alpha activity, a separate alpha measurement should be made to determine the alpha contribution to the beta measurement.

15.3.5 Beta Particle Counter

The end-window Geiger-Mueller tube and the internal proportional gas-flow chambers are the two most prevalent types of detectors. Other types of detectors include scintillators and solid-state detectors. The material used in the construction of the detector and its surroundings should contain a minimal level of detectable radioactivity. If the detector is of the window-type, the window thickness may be used in calculating beta-ray attenuation; however, direct calibration of the entire counting system with standards is recommended. The manufacturer should provide all settings and data required for reliable and accurate operation of the instrument. Detectors requiring external positioning of the test sample should include a support of low-density material (aluminum or plastic), which ensures a reproducible geometry between the sample and the detector. Because different sample to detector geometries are convenient for differing sample activity levels, the sample support may provide several fixed positions ranging from 5 to 100 mm from the detector.

The detection capability for both Geiger-Mueller and proportional counters is a function of the background counting rate. Massive shielding or anti-coincidence detectors and circuitry, or both,

are generally used to reduce the background counting rate to increase the lower limit of detection (Friedlander et al., 1964). ASTM E181 covers the procedure for the calibration of beta particle counting detectors. An application of beta particle counting is given in ASTM E1005.

15.3.6 Associated Electronic Equipment

The high voltage power supply amplifier, scaler, and mechanical register normally are contained in a single chassis. The power supply and amplifier sections are matched with the type of detector to produce satisfactory operating characteristics and to provide sufficient range in adjustments to maintain stable conditions. The scaler should have a capacity for storing and visually displaying at least 9×10^5 counts. The instrument should have an adjustable input sensitivity matched to that of the detector, and variable high voltage power supply—an adjustable power supply and meter are unnecessary for liquid scintillation systems. Counting chambers of Geiger-Mueller and proportional counters contain a suitable counting gas and an electrode. Counting rates that exceed 200 cps should be corrected for dead time loss when using a Geiger-Mueller tube. As the applied voltage to the electrode is increased, the counting chamber exhibits responses that are characteristic of a particular voltage region. At low voltages of the order of 100 V, there is no multiplication of the ionization caused by a charged particle. At voltages approaching 1,000 V, there is appreciable amplification of any ionization within the counting chamber; however, the size of the output pulse is proportional to the amount of initial ionization. When operated in this voltage region, the device is known as a proportional counter. Usually, there is a region at least 100 V wide, known as a plateau, wherein the count rate of a standard is relatively unaffected. The operating voltage for proportional counters is selected to approximate the middle of this plateau in order to maintain stable responses during small voltage shifts. The plateau region is determined by counting a given source at voltage settings that differ by 25 or 50 V. The number of counts at each setting is recorded, and the resultant counts versus voltage are plotted. Voltage plateau curves are to be re-measured periodically to ensure continued instrument stability, or whenever an instrument malfunction is indicated. If the voltage is increased beyond the proportional region into the 1,500 to 2,000 V region, the pulse size increases and the dependence on the initial ionization intensity disappears. This is the beginning of the Geiger counting region, where a single ion pair produces the same large pulse as an intense initial ionization.

In order to eliminate alpha particle interferences a thin absorber between the sample source and the detector can be used. The absorber diameter should exceed that of the detector window. The absorber should be placed against the window to minimize beta particle scatter. Any absorber that stops alpha particles will also attenuate low energy beta particles somewhat. For example, an aluminum absorber of 7 mg/cm^2 will absorb 48 percent of beta particles of 350 keV maximum energy. Chemical separation of the alpha and beta particle emitters produces a higher degree of

accuracy for internal detector measurements. Published information on beta particle absorption (Friedlander et al., 1964) should be used as a guide for use of an absorber. In liquid scintillation spectra, the alpha component appears as a peak on the beta continuum and thus provides a basis for resolving the two (Bogen and Welford, 1971).

15.4 Gamma Counting

15.4.1 Introduction

This section covers the non-destructive measurement of gamma-ray radioactivity. Since gamma radiation is a penetrating form of radiation, it can be used for non destructive measurements of samples of any form and geometry as long as standards of the same form are available and are counted in the same geometry to calibrate the detector. Because of this penetrating nature, attenuation, because of variations in sample density or sample thickness, although usually not significant, can be mathematically corrected.

When a standard cannot be obtained in the matrix and density of samples being counted, a correction for the different absorption in the matrices should be made (Modupe et al., 1993). Photons interact with matter in one of three ways: photoelectric, where all energy is transferred; Compton scattering, where only part of the energy is transferred; and pair production, where the energy creates a positron-electron pair. When the positron annihilates the electron, two 511 keV photons are emitted. Figure 15.1 shows the relative probability of each of the three predominant photon interactions with germanium.

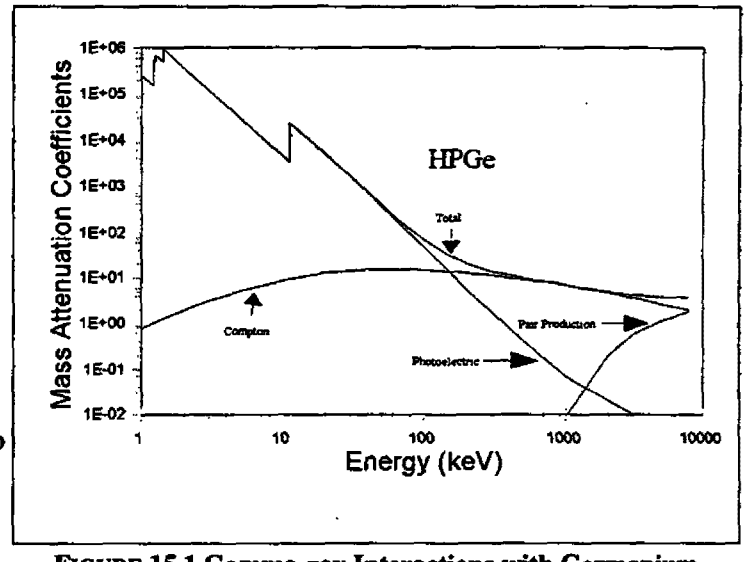


FIGURE 15.1 Gamma-ray Interactions with Germanium

Since different nuclides emit distinct and constant spectra of gamma radiation, the use of an energy discriminating system provides identification and measurement of all the components present in a mixture of radionuclides. General information on gamma-ray detectors and gamma counting is covered in the literature (Friedlander et al., 1964, and ICRU, 1994). Recent applications of gamma counting are given in several ASTM Test Methods (ASTM C758, C759, D3649).

Gamma counting is generally carried out using solid detectors since a gas-filled detector will not provide adequate stopping power for energetic gammas. In solids such as NaI(Tl) or CsI, the gammas interact by excitation of atoms and energy is transferred to orbital electrons and then released as light photons when the orbits are refilled. These scintillations are easily detected and amplified into useable electrical pulses by a multiplier phototube. The NaI(Tl) detector is the recommended detector for gross gamma counting because of its high efficiency and room temperature operation.

In semiconductor detectors such as Si(Li) and high-purity germanium semiconductors (HPGe), the gamma photons produce electron-hole pairs and the electrons are collected by an applied electrical field. A charge-sensitive preamplifier is used to detect the charge transferred and produce a useable electrical pulse. The semiconductor detectors are widely used in gamma spectrometry.

The output pulses from the multiplier phototube or preamplifier are directly proportional to the amount of energy deposited, which could either be total and included in the photopeak, or fractional and included in the continuum or escape peaks, in the detector by the incident photon. The pulses may be counted using a scaler or analyzed by pulse height to produce a gamma-ray spectrum.

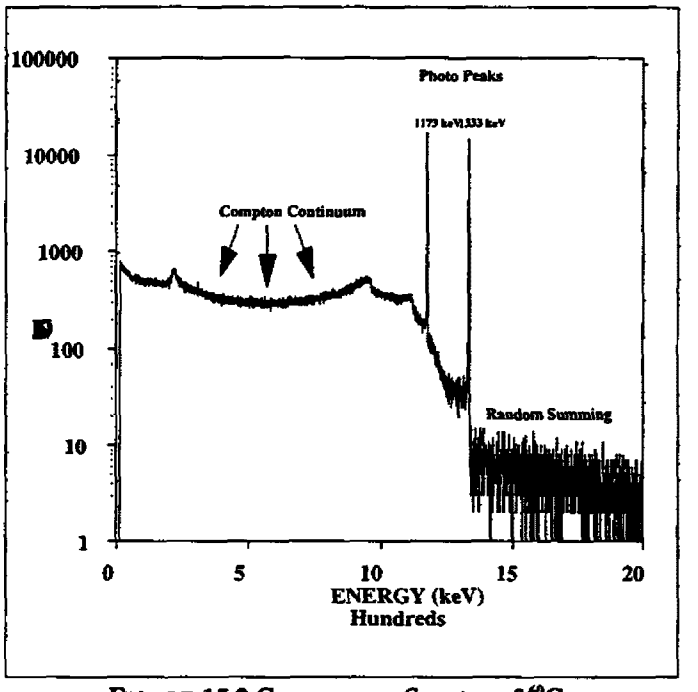


FIGURE 15.2 Gamma-ray Spectra of ^{60}Co

Gamma photons interact with the detector by three distinct processes. The photo-electric effect results in complete absorption of the photon energy and produces the full energy or photopeak shown. The Compton effect results in a partial absorption of the photo energy and a scattered photon of lower energy results. The scattered photon carries energy away and the Compton continuum results (Figure 15.2). The third interaction is pair production, which occurs at energies above 1,022 keV and results in the conversion of the photon to mass as an electron-positron pair. The electron and positron give up their kinetic energy to the detector and the resulting electron joins the electron population of the detector; the positron, however, is annihilated in combining with an electron and produces two gamma

423 photons of 511 keV each. One or both of the 511 keV photons may escape from the detector
424 without interacting and the single escape and double escape peaks result.

425 The Comptons, from a higher energy photon, always present an interference problem in the
426 counting of gamma photons and appropriate corrections should be made for this effect. Pair
427 production can also be considered as an interference since the escape peaks may have an energy
428 equal to the lower energy gamma of interest. The Compton and pair production effects can be
429 very significant interferences and should be corrected.

430 The change of the absorption coefficient with gamma energy results in a wide variation of
431 detection efficiency. The detection efficiency falls rapidly as gamma energy increases for a fixed
432 size of detector. Two other important effects are seen as a result of the variation of the absorption
433 coefficient; firstly, low energy photons may be absorbed in massive samples as sample thickness
434 increases, such as large bottles of water, and erroneous results may be obtained. A similar
435 absorption effect is seen in HPGe systems where the can around the detector acts as an absorber
436 for very low-energy gammas and the efficiency passes through a maximum usually around 100
437 keV. The second result is that for low energy gammas a thin detector may be as efficient as a
438 much thicker one since the low-energy gammas are easily stopped in the thin detector.
439 Additionally, thin detectors will have better low energy detection limits because of reduced
440 background interactions.

441 Because of this variation in efficiency and the possible interferences from other activities, gross
442 gamma counting is only reliable when used to compare standards and samples of the same
443 nuclide. The use of gross gamma monitoring systems should be avoided when possible and, in all
444 cases, proper allowance should be made for the lack of accuracy.

445 At high count rates, random sum peaking may occur. Two absorptions may occur within the
446 resolving time of the detector and electronics and are summed and seen as one pulse. For a
447 detector of resolving time, t, and a count rate of A counts per unit time, the time window
448 available for summing is 2At (since the count summed could occur as early as t before or as late
449 as t after the other count) and the probability of another count at any time is simply A. Therefore,
450 the sum count rate will be $2A^2t$ in unit time. Random summing is strongly dependent on the
451 count rate A and, if summing occurs, it can be reduced by increasing the sample to detector
452 distance. Modern electronics, both conventional analog and digital (preamplifiers, amplifiers, and
453 analog-to-digital converters) are capable of processing 100,000 cps without any significant lose
454 of resolution. This is because of the very short time constants (resolving time) these systems are
455 capable of producing. Over all detector performance can be affected by count rate because
456 reduced time constants are required which will cause some loss of resolution. When a photon

interaction takes place (an event is detected), charge carriers in the form of holes and electrons are produced. The electrical field produced by the detector's high voltage bias supply causes these carriers to be swept toward the P and N electrodes of the detector. The time it takes the carriers to travel to the electrodes is called the "charge collection time." At very high count rates the detector continues collecting events but the data is not valid. If a second (or third) event takes place while the first set of charge carriers are still in transit, the energy from the two events get added together. Therefore, if a 2,000 keV event arrives while a 1,000 keV event is in transit, the detector would "see" a single 3,000 keV event, producing a random sum peak on pulse pileup. When the detector starts reporting more sum peaks than valid events, you have exceeded its count rate capability. Random pulse summing or pileup can also cause peak shape and risetime problems. But the real upper limit to a detector throughput is pulse summing. This problem can be reduced or eliminated by either reducing the number of events the detector "sees" by moving the sample further away, collimate the detector, or use a smaller, less efficient detector; the smaller the detector the shorter the charge collection time, which means a higher count rate limit. Peak shifts may also occur with high count rates and short time constants. Another factor that will affect high count rate performance is improper setting of the amplifier pole zero. Improper setting of the pole zero with either under or over shooting of input pulse will effect peak resolution.

Well counters that have very high efficiencies are prone to summing since, for a given source strength, the count rate is higher than for a detector of lower efficiency. For moderate and high-source strengths, the trade-off is a poor one and the well counter is best suited for low-level work where its high efficiency is an important advantage.

Cascade summing may occur when nuclides that decay by a gamma cascade are counted. Cobalt-60 (^{60}Co) is an example; 1,173.2 keV and 1,332.5 keV from the same decay may enter the detector and be absorbed, giving a 2,505.7 keV sum peak. Another example of Cascade summing occurs when counting sodium-22 (^{22}Na) close to the detector (see Figure 15.3). Cascade summing may be reduced and eventually eliminated by increasing the source-to-detector distance.

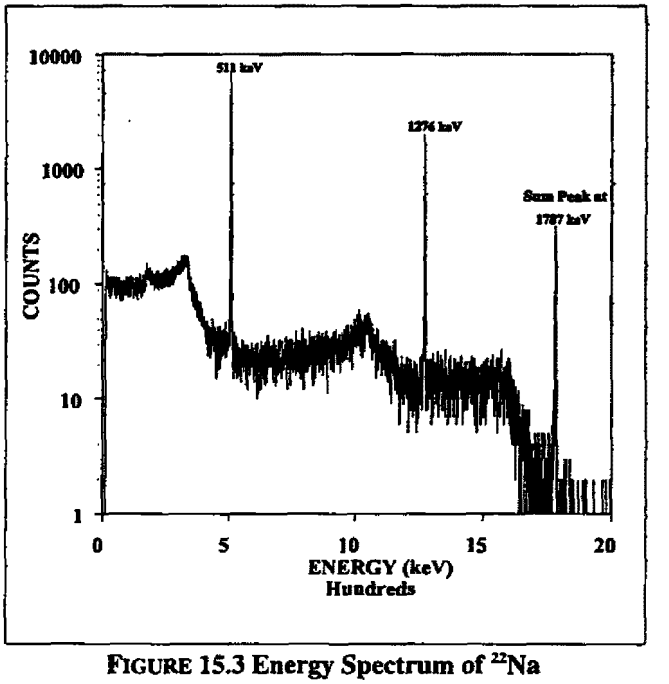


FIGURE 15.3 Energy Spectrum of ^{22}Na

The resolution of a gamma detector is the effective limit to its utility even when complex data reduction methods are used. A typical 76x76 mm NaI(TI) detector will give full-width half-maximum (FWHM) of approximately 60 keV at 661.6 keV gamma energy and approximately 90 keV at 1,332.5 keV gamma energy.

15.4.2 Energy Efficiency Relationship

Because of the rapid falloff in gamma absorption as gamma energy rises, the detection efficiency shows a similar effect. Figure 15.4 shows a typical efficiency vs. energy plot of a 70 percent HPGe p-type, a 35 percent HPGe n-type, and HPGe well detectors of 122 cm^3 with a vespel well and 320 cm^3 with a Mg well. The portion of the curve for n-type and well detectors at low energies shows that as the absorption coefficient increases geometry becomes the limiting factor. The maximum efficiency for both co-axial detectors is well below 50 percent due to the presence of a beta absorber, the containment of the detector and the geometry effect. The p-type detector shows significant low energy efficiency drop off because of the absorption of gamma rays in the detector's inactive Ge dead layer. The well detector shows excellent efficiency below 100 keV because of the geometry effect and absence of an attenuating germanium dead layer. The 76x76 mm NaI(TI) detector is the most widely used size. A large amount of data are available in the open literature on both the use and results obtained with detectors of this size. Heath (1964) has written a comprehensive review and supplied many gamma-ray spectra in both graphical and digital form.

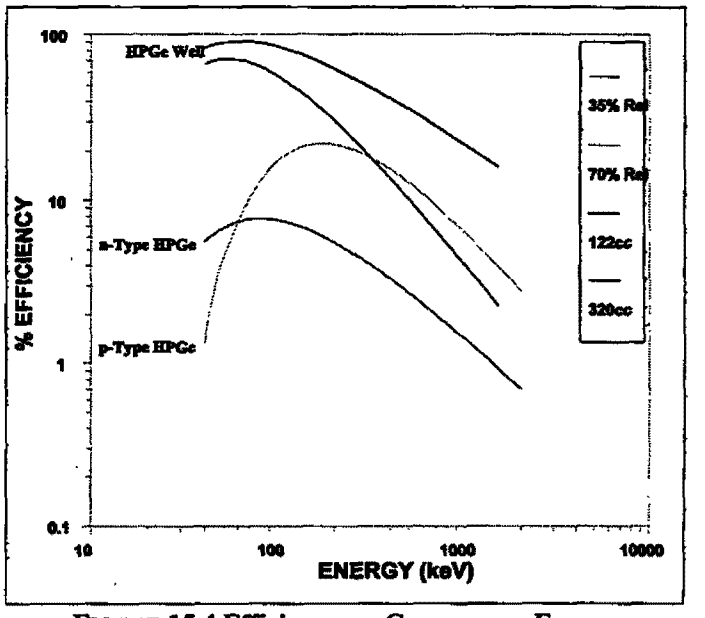


FIGURE 15.4 Efficiency vs. Gamma-ray Energy

Other sizes of detectors may be used. However, the following should be noted: smaller detectors, such as 38x38 mm, will give efficiencies that are low and fall off more rapidly as gamma energy increases. Small or thin detectors are useful for the measurement of low-energy gammas since they are less responsive to high-energy gammas and the interference from Compton effects is reduced. This will result in a lower background.

Larger detectors will give higher efficiencies and less falloff as gamma energy increases. Larger detectors are useful for situations where the highest attainable efficiency is desired and for the assembly of complete absorption detectors. The increase in efficiency is accompanied by an increased background count rate and an increase in the probability of summing in the detector.

Well detectors will give very high efficiencies, up to about 80 percent for low and moderate energy gammas. The well detector is useful for low levels of activity and the background of a well detector is essentially the same as that of a plain cylindrical detector of the same overall dimensions. Summing becomes a definite problem at high activities since both random and cascade summing result from the high efficiencies and the high geometry of the well detector.

Detector efficiency will also vary as a function of sample geometry. Table 15.1 gives counting efficiencies obtained with various sample geometries for a 55 percent HPGe detector.

TABLE 15.1 Typical Percent Gamma-ray Efficiencies for a 55 Percent High-Purity Germanium Detector* with Various Counting Geometries

ENERGY (keV)	FILTER PAPER	50 cm^3 PLANCHET	90 cm^3 AL CAN	600 cm^3 MARINELLI BEAKER
60	15.6	14.6	11.6	5.0
88	15.2	14.2	11.3	7.4
122	15.1	12.6	10.2	8.4
166	12.0	9.6	8.0	7.9
279	9.3	7.4	6.0	6.1
392	7.2	5.5	4.5	4.8
514	5.4	4.2	3.5	3.8
662	4.7	3.6	3.0	3.1
835	3.9	2.9	2.4	2.7
898	3.1	2.4	2.1	2.2
1115	3.0	2.3	1.9	2.1
1173	2.6	2.0	1.7	1.8
1333	2.3	1.8	1.5	1.6
1836	1.7	1.3	1.2	1.3

*Although the counting efficiencies listed above were obtained with a 55 percent (relative to a 3x3 inch NaI detector) HPGe detector, the calculation of counting efficiencies by extrapolation for detectors with different relative efficiencies is not possible. This is because detectors with the same relative efficiency may be of significantly different dimensions thus producing a detector/sample solid angle very different than what was used to prepare this table.

15.4.3 Sodium Iodide Detector Assembly

A cylindrical 76x76 mm NaI detector is activated with about 0.1 percent thallium iodide, with or without an inner sample well, optically coupled to a multiplier phototube, and hermetically sealed in a light-tight container. The NaI(Tl) crystal should contain less than 5 ppm of potassium and be free of other radioactive materials. In order to establish freedom from radioactive materials, the manufacturer should supply a gamma spectrum of the background of the detector between 0.08 and 3,000 keV. The resolution of the detector for the 662 keV gamma from ^{137}Cs decay should be less than 50 keV FWHM or less than 7 percent when measured with the source in contact with the end cap.

The following components are required for a complete NaI(Tl) gamma-ray spectrometry system:

High-Voltage Power Supply	500 to 2,000 V dc regulated to 0.1 percent with a ripple of not more than 0.01 percent
Preamplifier	Linear amplifier system to amplify the output from the multiplier phototube to a maximum output of 10 V.
Analyzer with Scaler and Timer	A single-channel discrimination system will accept all or any part of the output from the amplifier and pass it to the scaler. Any pulses lying outside the preset limits are rejected. The lower limit is usually referred to as the *threshold* and the difference between the two limits is the *window*. Sample mounts and containers may consist of any reproducible geometry container that is commercially available. Other considerations are cost, ease of use, disposal, and effective containment of radioactivity for the protection of the workplace and personnel from contamination.
Beta Absorber	A beta absorber of 3 to 6 mm of aluminum, beryllium, or poly(methyl methacrylate) should completely cover the upper face of the detector to prevent betas from reaching the detector.

15.4.4 High Resolution Germanium Detectors

High resolution germanium detectors are produced from very high purity material, the required level of impurities in the detector crystal is usually less than 10^9 atom/cm^3. Any type of germanium—either planar, co-axial or well-configuration—cannot be operated at room temperature because of the large thermally induced leakage current that results. These detectors should be cooled in order to reduce the thermal generation of charge carriers (thus reverse leakage current) to an acceptable level. Otherwise, leakage current induced noise reduces the energy resolution of the detector. The detector is mounted in a vacuum chamber which is attached to or inserted into an liquid nitrogen (LN2) dewar or an electrically powered cooler. The sensitive detector surfaces are thus protected from moisture and condensation contaminants.

The boiling point of liquid nitrogen (77 °K) is usually taken advantage of to reduce the operating temperature of the detector. Since germanium detectors can be operated at temperatures as high as 130 °K, mechanical closed-cycle refrigerators can also be used. These systems can cool a detector to as low as 50 °K. Therefore, with proper thermal control the detector can be cooled to its optimum operating temperature. The required preamplifier is normally included as part of the cryostat. In this configuration the preamplifier can also be cooled to reduce electronic noise.

HPGe detectors are preferred for the analysis of complex gamma-ray spectra involving many nuclides and peaks. However, for samples with only a few nuclides, the complexity of an HPGe system may not be cost effective. The calibration of germanium detectors is given in ASTM E181.

15.4.5 Low Background High Resolution Germanium Detectors

Environmental samples requiring the lowest possible minimum detection analyses (MDAs) should be counted with large high efficiency germanium detectors in low background cryostats. Most of the background from naturally occurring radionuclides such as ^{40}K from building materials, radon decay products, and cosmic rays can be reduced by proper shielding. However, naturally occurring ^{235}U, ^{238}U, ^{232}Th, and anthropogenic ^{137}Cs and ^{60}Co may be present in cryostat materials. With careful selection and substitution of materials, low background gamma-ray systems can be fabricated. Germanium crystal mountings and detector end caps have been fabricated with magnesium to eliminate aluminum contaminated with radioactive thorium isotopes. Figures 15.5 and 15.6 show shielded background spectra obtained with 56 percent germanium detectors in standard and extra low background cryostats.

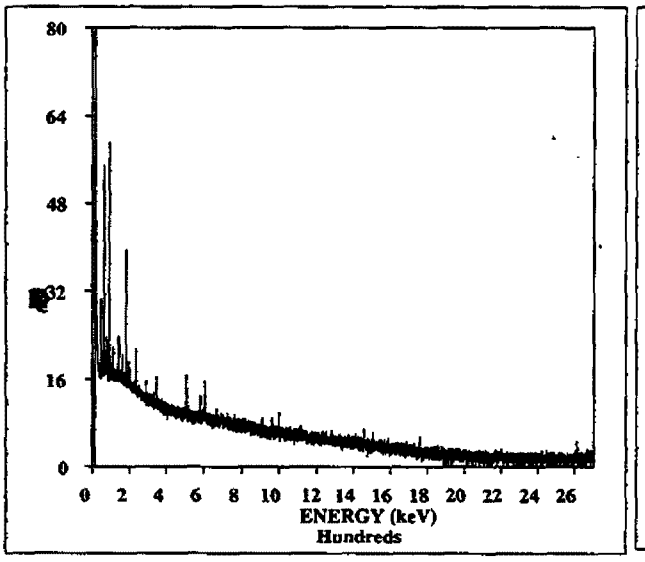


FIGURE 15.5 Standard Cryostat HPGe Background Spectrum

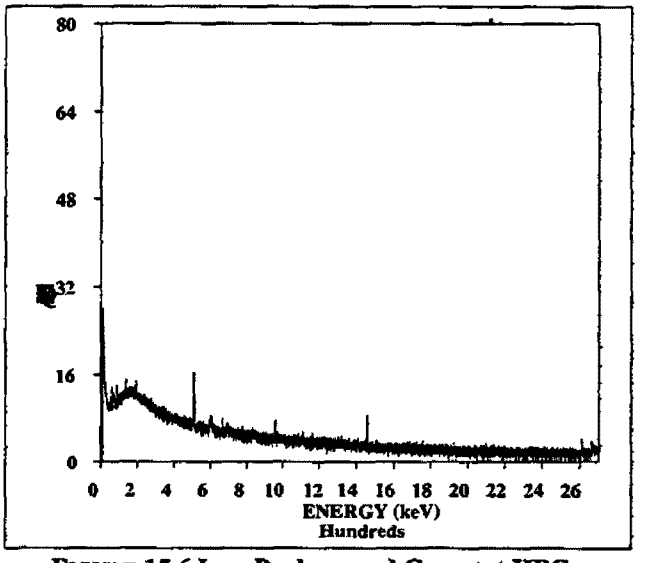


FIGURE 15.6 Low Background Cryostat HPGe Background Spectrum

15.4.6 High Resolution Detectors for Low Energy Spectrometry

High resolution low gamma-ray energy detectors are available in various configurations. The commonly used ones are either high purity germanium or silicon. The various detector types include: planar (Ge or Si), low-energy germanium (LEGe), reverse-electrode germanium (REGe) and extended-range germanium (XtGe). These detectors are equipped with beryllium entrance windows to reduce attenuation. These detectors are especially useful for measuring nuclides that emit gamma or X-rays from a few keV to about 150 keV.

15.4.7 CsI(Tl) Detectors

CsI(Tl) crystals have the highest light output of all known scintillators. However, because light output is not well matched to the sensitivity of the photocathode of a multiplier phototube, the yield for gamma rays is only 45 percent of the efficiency of NaI(Tl). With the proper electronics, CsI(Tl) detectors can be used for α-particle energy discrimination.

15.4.8 CdZnTe Detectors

These gamma-ray detectors, in addition to only being produced in very small volumes, do not have energy resolutions as good as HPGe but are better than NaI(Tl). Their greatest advantage is

their ability to operate at room temperature. Because of their small size and resulting low gamma-ray detection efficiency, they are useful for the analysis of very high level sources.

15.4.9 BGO Detectors

Because bismuth germanate ($Bi_4Ge_3O_{12}$)is a high Z, high density (7.13 gcm^3), scintillation material, it is a very efficient gamma-ray absorber. Although BGO crystals a have very good peak-to-Compton ratio, their effective efficiency is only 10 to 15 percent as good as a NaI(Tl) crystal. However, BGO is a relatively hard, rugged, non-hygroscopic crystal which does not cleave or absorb any significant amount of the scintillation light. The crystal housing does not require hermetic air-tight sealing. These crystals are useful in applications where high photofraction is required.

15.5 Spectrometry Systems

This section will present a number of different type of detector systems commonly use for gamma-ray spectrometry.

15.5.1 Alpha/Gamma Coincidence Systems

Alpha/Gamma Coincidence Systems have been used for the direct measurement of ^{224}Ra and ^{226}Ra. The counting technique is based upon the coincidence measurement of the characteristic particle-photon emissions of these isotopes. Silver activated zinc sulfide for alpha detection is combined with a NaI well for gamma-ray detection (McCurdy, 1981).

15.5.2 Beta/Gamma Coincidence Systems

Many radionuclides remain in an excited state after what may be considered beta decay. This results in the emission of a gamma ray as the decay process goes to the ground state. A beta/gamma coincidence system will have significantly improved lower limit of detection over a beta or a gamma counting system because of its very low background. Systems have been designed with both 2-π and 4-π geometry (McCurdy et al., 1980).

15.5.3 Gamma/Gamma Coincidence Systems

These counting systems can provide extremely low backgrounds and are very useful for analyzing those radionuclides that decay with cascading (coincident) gamma rays. The systems usually consist of two large NaI(Tl) detectors with a surrounding active anti-coincidence shield

of either NaI(Tl) or plastic phosphor. However, HPGe detectors have also been used in place of the two large NaI(Tl) detectors. Only gamma-ray pulses that are detected in both of the primary detectors at the same time (coincident) and not in the active shield are recorded. Even though these systems can be large, because of the shielding requirements for two detectors and an active annulus, and require complex electronics, the improvement in lower limit of detection for certain radionuclides is worth the investment (Perkins, 1965; Sanderson, 1969).

15.5.4 Photon-Electron Rejecting Alpha Liquid Scintillation Systems

Another technique for the analysis of alpha emitting radionuclides combines liquid scintillation counting with pulse shape discrimination to significantly reduce background counts from photo-electrons produced by ambient background gamma rays and to eliminate interferences from beta emitters in the sample/scintillation cocktail. Pulse shape discrimination electronically selects only pulses produced by alpha particles because of their longer decay times in the scintillation solution. Typical alpha peak resolutions are about 5 percent. Typical detectable activities for alpha emitters such as ^{234}U and ^{241}Am are 0.0037 and 0.37 Bq (0.1 and 10 pCi).

15.6 Special Instruments

This section covers some radiation detection instruments and auxiliary equipment that may be required for special application in the measurement of radioactivity.

15.6.1 4-π Counter

The 4-π counter is a detector designed for the measurement of the absolute disintegration rate of a radioactive source by counting the source under conditions that approach a geometry of 4-π steradian. Its most prevalent use is for the absolute measurement of beta emitters. For this purpose, a gas-flow proportional counter is commonly used. 4-π counting systems consist of two hemispherical or cylindrical chambers whose walls form the cathode, and a looped wire anode in each chamber. The source is mounted on a thin supporting film between the two halves, and the counts recorded in each half are summed.

Gamma-ray and hard X-ray counters with geometries approaching 4-π steradian can be constructed from both NaI(Tl) or germanium crystals in either of two ways. A well crystal (that is, a cylindrical crystal with a small axial hole covered with a second crystal) will provide nearly 4-π geometry for small sources, as will two solid crystals placed very close together with a small source between them. The counts from both crystals are summed as in the gas-flow counter. The deviation from 4-π geometry can be calculated from the physical dimensions. For absolute

679 gamma-ray counting, the efficiency of the crystal for the gamma energy being measured and the
680 absorption in the detector end cap should be taken into account. The liquid scintillation counter is
681 also essentially a 4-π counter for alpha and beta particles, since nearly all the radiations are
682 emitted into and interact with the detecting medium.

683 **15.6.2 Low-Geometry Counters**

684 This type of instrument is particularly useful for the absolute counting of alpha particles. The
685 alpha emitter, in the form of a very thin solid source, is placed at a distance from the detector
686 such that only a small fraction (<1 percent) of the alpha particles are emitted in a direction to
687 enter the counter. This solid angle is obtained from the physical measurements of the instrument.
688 The space between the source and the detector is evacuated to eliminate the loss of alpha
689 particles by absorption in air. The detector can be any counter that is 100 percent efficient for all
690 alpha particles that enter the sensitive volume—a gas-flow proportional counter with a window
691 that is thin (approximately 1 mg/cm^2) compared to the range of the alpha particles or the
692 semiconductor alpha detector with a 1 mg/cm^2 covering. The advantages of this instrument for
693 absolute alpha counting are that the effect of absorption of alpha particles in the source itself is
694 kept to a minimum since only particles that travel the minimum distance in the source enter the
695 detector (particles that have longer paths in the source are emitted at the wrong angle), and back-
696 scattered alpha particles (those that are emitted into the source backing and are reflected back up
697 through the source) lose sufficient energy so that they cannot enter the detector. One such
698 instrument is described in Curtis et al. (1955).

699 **15.6.3 Internal Gas Counters**

700 The internal gas counter is so named because the radioactive material, in the gaseous state, is
701 placed inside a counting chamber and thus becomes part of the counting gas itself. It is useful for
702 high-efficiency counting of weak beta- and X-ray emitting radionuclides. The radiations do not
703 have to penetrate a counter window or solid source before entering the sensitive volume of a
704 detector. The counter may be an ionization chamber, or it may be operated in the Geiger or
705 proportional mode. Most present-day instruments are of the latter type, and they generally take
706 the form of a metal or metal-coated glass cylinder as a cathode with a thin anode wire running
707 coaxially through it and insulated from the cylinder ends. A wire through the wall makes
708 electrical contact to the cathode. The counter has a tube opening through which it may be
709 connected to a gas-handling system for filling. The purity of the gas is important for efficient and
710 reproducible counting, particularly in the proportional mode.

711 In a modification of the internal gas counter, scintillation counting has been used. The inner walls
712 of the chamber are coated with a scintillation material and the radioactive gas is introduced. An
713 optical window is made a part of the chamber, and the counting is done by placing this window
714 on a multiplier phototube to detect the scintillations. This system is particularly useful for
715 counting radon gas with zinc sulfide as the scintillator. Additional details on internal gas
716 counting may be found in Watt and Ramsden (1964).

717 15.7 Spectrometers and Energy-Dependent Detectors

718 The availability of energy-dependent detectors (detectors whose output signal is proportional to
719 the energy of the radiation detected) that are easy to operate and maintain and have good
720 resolution makes it possible to measure not only the total activity of a radioactive sample but the
721 energy spectrum of the nuclear radiations emitted. Nuclear spectrometry is most useful for alpha
722 particles, electromagnetic radiation (gamma and X-rays), and conversion electrons, since these
723 radiations are emitted with discrete energies. Beta spectra have more limited use since beta
724 particles are emitted from a nucleus with a continuous energy distribution up to a characteristic
725 maximum (E- max), making a spectrum containing several different beta emitters difficult to
726 resolve into its components. The advantages of spectrometric over total activity measurements of
727 radioactive sources are increased selectivity, detection limit , and accuracy because nuclide
728 identification is more certain, interference from other radioactive nuclides in the sample is
729 diminished or eliminated, and counter backgrounds are reduced since only a small portion of the
730 total energy region is used for each radiation.

731 The detectors for alpha spectra are gridded ion-chambers and silicon semiconductor detectors.
732 Gridded ion-chambers are no longer available commercially and should be constructed by the
733 user. A variety of semiconductor detectors for alpha spectrometry are commercially available.
734 These detectors have essentially replaced ion-chambers, although the chambers have the
735 advantages of high efficiency (nearly 50 percent) for large-area sources.

736 Silicon alpha particle detectors have a depletion region which is formed by applying a high
737 voltage bias. The electric field produced collects the electron-hole pairs produced by incident
738 alpha particles. Either surface barrier or passivated ion-implanted silicon are commonly used for
739 spectrometry.

740 The principal detectors used for gamma-ray spectrometry are thallium-activated sodium iodide
741 scintillation crystals, NaI(Tl), and high purity germanium semiconductors, HPGe. HPGe
742 detectors are available in n-type and p-type germanium. P-type germanium detectors have dead
743 layers which produce entrance windows from 500 to 1,000 μm thick. On the other hand, n-type

detectors have extremely thin entrance windows of about 0.3 μm. These n-type detectors when housed in an end cap with a beryllium window are excellent for measuring both low energy and high energy (3 to 10,000 keV) gamma rays. However, applications which require the best possible energy resolution, peak shape, and efficiency for gamma-ray measurements above 80 keV, p-type HPGe is the detector material of choice.

For X-rays and very low-energy gamma rays, lithium-drifted silicon semiconductor Si(Li), planar germanium, and gas-filled thin window (approximately 1 mg/cm^2) proportional counters are used.

The electronic version of Heath's (1964) Ge(Li) and Si(Li) Detector Gamma-ray Spectrum Catalogue is available in two forms. The document is on the Web at http://id.inel.gov/gamma; it is also available on a CD-ROM.

The portion of the crystal end cap through which gamma rays enter is normally thinner, or constructed of a low-Z material, like beryllium or magnesium, than the rest of the package in order to reduce low-energy attenuation. Sodium iodide crystals are available in a large range of sizes and shapes, from thin crystals for X-ray analysis and small 25 by 25 mm cylinders to hemispheres and cylinders over 300 mm in diameter. Information on the types of crystal packages and mountings is available from the manufacturers.

A complete NaI(Tl) detector spectrometer requires a high-voltage power supply for the phototube (usually operated at 600 to 1,000 V), a preamplifier, linear amplifier, pulse-height analyzer, and output recorder. Because NaI(Tl) detectors cannot resolve gamma-ray energies that are only a few keV apart, a least-squares computer program should be used to quantify a complex gamma-ray spectrum.

Germanium and silicon detectors are junction-type semiconductor devices. With silicon detectors, a sensitive region is produced by drifting lithium under the influence of an electric field at an elevated temperature (100 to 400 °C) into the crystal. The crystal then functions as a solid ion chamber when a high voltage is applied. Today, germanium detectors are made with very high purity material that does not require lithium drifting. In order to obtain high resolution, these detectors should be operated at low temperatures to reduce thermal noise. At room temperature, sufficient free electrons will be present in the crystal to obscure the measurement of gamma and X-rays. Consequently, the detectors are operated at liquid nitrogen temperatures by a cryostat consisting of a metallic cold-finger immersed in a Dewar flask containing liquid nitrogen or mechanically refrigerated.

The electronic components required to obtain spectra are similar to those for NaI(Tl) detectors, except that because smaller pulses should be measured, high-quality electronics should be used. A complete HPGe system includes a high-voltage bias supply for the detector, a preamplifier, amplifier (usually charge-sensitive), pulse height analyzer, and recording device. With the exception of extremely complex spectra, most high resolution spectra can be quantified by simple integration of full energy gamma-ray peaks.

The resolution of gamma-ray detectors is usually specified in terms of its FWHM. Detector resolution, expressed in percent, improves with increasing energy and for NaI(Tl) detectors and is usually determined from the 662 keV gamma ray emitted in the decay of ^{137}Cs. This is shown graphically in the gamma-ray spectrum in Figure 15.7. For HPGe detectors, ^{60}Co is measured 25 cm above the detector end cap. Quality sodium iodide crystals have resolutions in the range of 6.5 to 7 percent for ^{137}Cs. Detection efficiency for the same geometry and window thickness is a function of several parameters and much published information on efficiencies for various energies, detector sizes, source-to-detector distances, and other variables is available (Crouthamel et al., 1970). The efficiency for gamma-ray detection is expressed as full energy peak efficiency; the fraction of incident gamma rays that give a full-energy peak for a particular source-detector configuration. For a 102 mm thick NaI(Tl) crystal, with the source on the surface (zero distance), this fraction is approximately 0.24 for the 661.6 keV gamma ray of ^{137}Cs and approximately 0.14 for the 1,332.5 keV gamma ray of ^{60}Co. The peak-to-valley or peak-to-Compton ratio is the ratio of counts at the maximum height of the full-energy peak to the counts at the minimum of the Compton continuum. A high ratio indicates narrow peaks, that is, good resolution, for that particular energy.

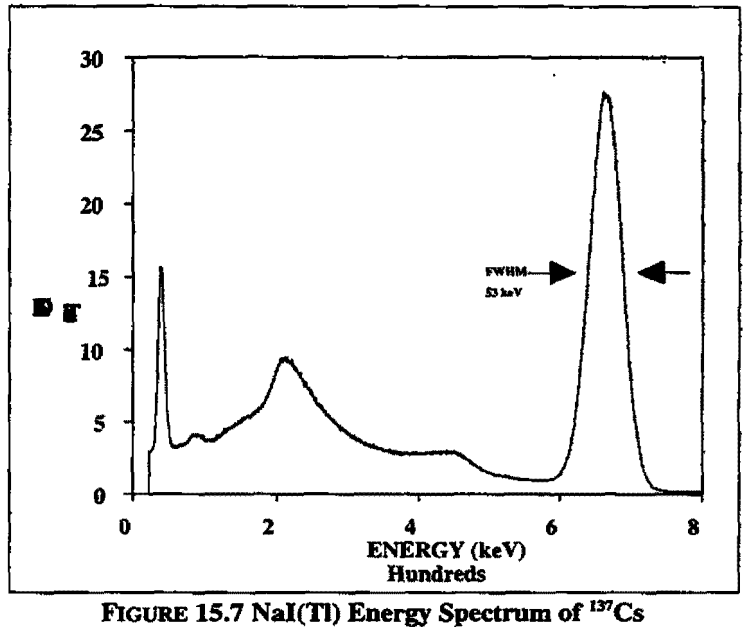


FIGURE 15.7 NaI(Tl) Energy Spectrum of ^{137}Cs

The efficiency specification of a HPGe detector is expressed by comparing its ^{60}Co, 1,332.5 keV efficiency at 25 cm with that of a 76x76 mm cylindrical NaI(Tl) detector at the same distance.

Photopeaks are spread over a much smaller energy range in germanium than in sodium iodide, the background under the peak is much less (Figure 15.8). This means that for small sources of moderately energetic gamma rays, germanium is more sensitive than sodium iodide.

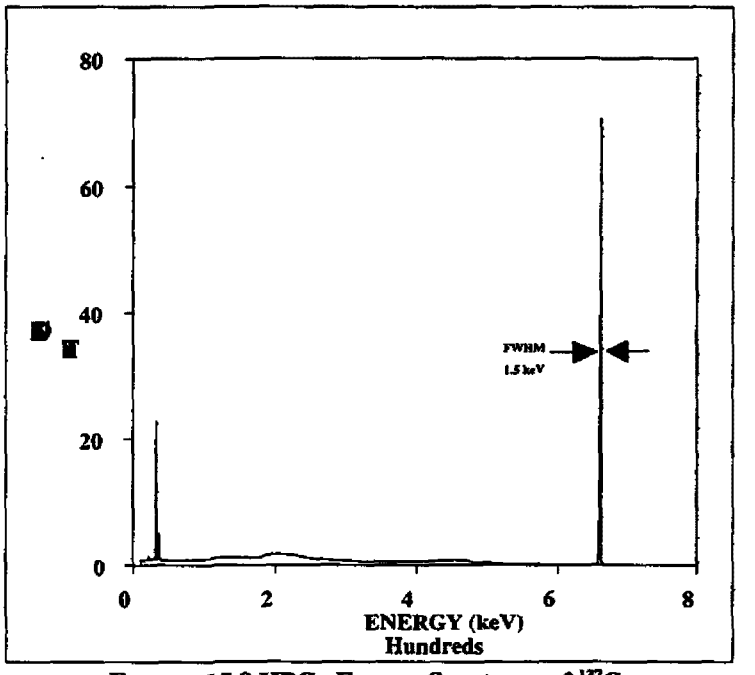


FIGURE 15.8 HPGe Energy Spectrum of ^{137}Cs

Typical specifications for a germanium gamma-ray detector could include but should not be limited to the following:

DETECTOR: The gamma-ray detector should consist of High-Purity n-type germanium.

SIZE: The germanium crystal should be at least 5.5 cm in diameter and at least 7.0 cm long.

EFFICIENCY: The relative counting efficiency compared to a 3"x3" NaI detector at 25 cm for ^{60}Co (1,332 keV) should be equal to or better than 50 percent.

RESOLUTION: The resolution (FWHM) of the detector should be equal to or better than 2.2 keV at 1,333 keV (^{60}Co). The resolution (FWHM) at 122 keV (^{57}Co) of the detector should be equal to or better than 1.0 keV. The detector resolution at FWTM should be equal to or better than 2 times the FWHM.

PEAK-TO-COMPTON RATIO: The peak-to-Compton ratio for 1,333 keV (^{60}Co) should be equal to or better than 50:1.

BACKGROUND: Low radioactivity materials should be used so that any full energy gamma-ray line (excluding 511 keV and 1,460 keV) present in a 1,000-minute background spectrum (100-2,000 keV) obtained in a graded 10 cm lead shield should not exceed 0.20 counts per minutes.

CONTACTS: The internal detector contacts should be DC-coupled ion implants so that low energy gamma-ray attenuation is avoided.

PREAMP: A low-noise, cooled field-effect transistor preamplifier should be used to provide the detector output signals.

CRYOSTAT: The cryostat should be constructed of low radioactivity materials throughout and should contain sufficient lead shielding in order to minimize radiation from the dewar or lower portion of the cryostat.

END CAP: The end cap should consist of a 20 mil beryllium window with 0.5 mm aluminum side walls and be no greater then 7.6 cm diameter (OD). This diameter should be maintained for at least 8 cm from the end cap. Below this point the outside diameter of the end cap may be increased. The top of the end cap should be between 95 and 102 cm above the outside base of the dewar.

TEMPERATURE: The cryostat should contain a temperature sensing circuit to provide high voltage shut down in order to prevent preamplifier damage in case of warm-up due to loss of liquid nitrogen.

Spectra of beta particles and conversion electrons can be obtained with sodium iodide and n-type HPGe detectors. A germanium detector with a volume of 120 cm^3 has an efficiency approximately 20 percent that of a 76x76 mm NaI(Tl) crystal. Larger HPGe detectors are available with relative efficiencies over 150 percent when compared with a 76x76 mm NaI(Tl) crystal.

Presently available germanium detectors have resolutions of 1.5 to 2.5 keV at 1,332.5 keV. The method used to measure the energy resolution is described in ANSI/IEEE 325. This greater resolution makes this detector the one of choice for gamma-ray spectrometry and cancels to some extent the higher efficiency available from sodium iodide. Since the pulses from a single semiconductor detectors sufficiently thick (a few centimeters) to absorb the particles completely. One disadvantage of sodium iodide detectors is their relatively thick entrance windows. Other semiconductor detectors have thin beryllium entrance windows and can be used for beta spectrometry.

Good spectra of low-energy beta particles, conversion electrons, and X-rays can be obtained with a gas-flow proportional Counter provided that a linear preamplifier is used. The resolution is intermediate between NaI(Tl) and HPGe. Organic scintillators, such as anthracene and polystyrene polymerized with scintillating compounds, are also useful for beta spectrometry.

They are packaged with a phototube in a manner similar to sodium iodide crystals. Liquid scintillation mixtures also give beta spectra, and the output of a commercial liquid scintillation counter is usually fed into a multichannel pulse-height analyzer to obtain a beta energy spectrum (Blanchard et al., 1960). A spectrum of ^{210}Pb, ^{210}Bi, and ^{210}Po in Figure 15.9 shows the resolution obtainable by liquid scintillation counting of aqueous samples in a dioxane-based solution. The ^{210}Bi curve is from a beta particle, and the ^{210}Po peak is from an alpha particle. Organic scintillators are preferable to sodium iodide for beta spectrometry because less back scattering occurs.

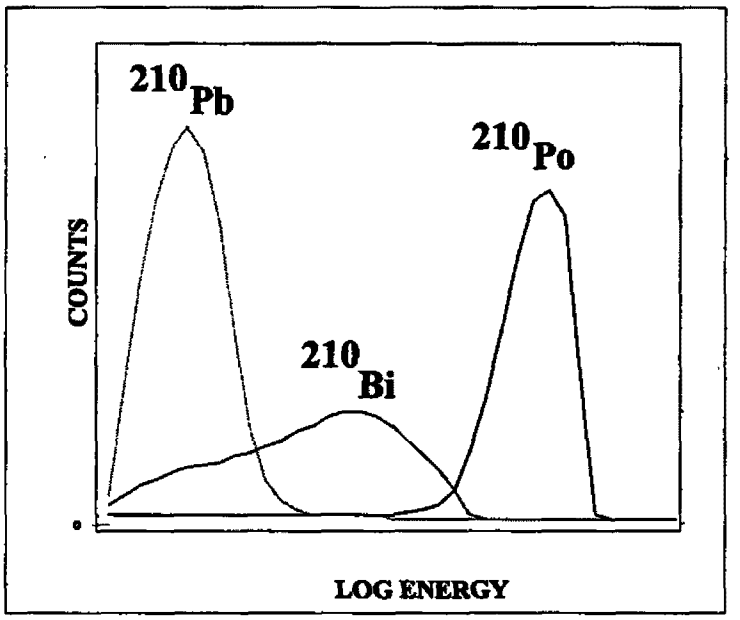


FIGURE 15.9 Spectrum of ^{210}Pb, ^{210}Bi, and ^{210}Po

15.7.1 Anti-Coincidence Counters

Substantial background reduction can be achieved in beta and gamma counters by surrounding or covering the sample detector with another detector also sensitive to beta or gamma radiation, and connecting them electronically so that any pulse appearing in both detectors at the same time is canceled and not recorded as a count. This is referred to as anti-coincidence shielding, and is recommended for obtaining very low backgrounds. This type of counter was used for many years in directional studies of cosmic rays, and was first applied to reducing the background of beta counters by Libby in his study of natural ^{14}C. The thick metal shielding (lead, iron, or mercury) ordinarily used to reduce cosmic-ray and gamma-ray background should also be present, and is placed outside the anti-coincidence shielding.

Anti-coincidence shielding of gamma-ray detectors operates in a similar way, and is particularly useful in reducing the Compton continuum background of gamma rays (Nielson, 1972). Gamma rays that undergo Compton scattering and produce a pulse in both the detector and the anti-coincidence shield are canceled electronically. Ideally, only those gamma rays that are completely absorbed in the sample detector produce a count that is recorded with the total energy of the gamma ray (full-energy peak). There are second-order effects that prevent complete elimination

of Compton scattering, but the improvement is substantial (Perkins, 1965, and Cooper et al., 1968).

15.7.2 Coincidence Counters

In coincidence counting, two or more radiation detectors are used together to measure the same sample, and only those nuclear events or counts that occur simultaneously in all detectors are recorded. The coincidence counting technique finds considerable application in studying radioactive decay schemes; but in the measurement of radioactivity, the principal uses are for the standardization of radioactive sources and for counter background reduction.

Coincidence counting is a very powerful method for absolute disintegration rate measurement (Friedlander et al., 1964; IAEA, 1959). Both alpha and beta emitters can be standardized if their decay schemes are such that β-γ, γ-γ, β-β, α-β, or α-X-ray coincidence occur in their decay. Gamma-gamma coincidence counting with the source placed between two sodium iodide crystals, is an excellent method of reducing the background from Compton scattered events. Its use is limited, of course, to counting nuclides that emit two photons in cascade (which are essentially simultaneous), either directly as in ^{60}Co, by annihilation of positrons as in ^{65}Zn, or by immediate emission of a gamma ray following electron capture decay. Non-coincident pulses of any energy in either one of the crystals will be canceled, including cosmic-ray photons in the background and degraded or Compton scattered photons from higher energy gamma rays in the sample. Thus, the method reduces interference from other gamma emitters in the sample. When two multichannel analyzers are used to record the complete spectrum from each crystal, singly and in coincidence, then the complete coincident gamma-ray spectrum can be obtained with one measurement. The efficiency for coincidence counting is low since it is the product of the individual efficiencies in each crystal, but the detection limit is generally improved because of the large background reduction (Nielsen and Kornberg, 1965). This technique is often referred to as two-parameter or multidimensional gamma-ray spectrometry.

Additional background improvement is obtained if the two crystals are surrounded by a large annular sodium iodide or plastic scintillation crystal connected in anti-coincidence with the two inner crystals. In this case a gamma ray that gives a pulse, but is not completely absorbed in one of the two inner crystals, and also gives a pulse in the surrounding crystal, is canceled electronically (Perkins, 1965, and Nielsen and Kornberg, 1965). This provides additional reduction in the Compton scattering background. Germanium detectors may be used in place of the inner sodium iodide crystals for improved resolution and sensitivities (Cooper et al., 1968). An example of an assay for plutonium content using passive thermal-neutron coincidence

939 counting is given in ASTM (C1207). Another example of passive thermal-neutron coincidence
940 counting using a moveable californium source is given in ASTM (C1316).

941 15.8 Shielding

942 The purpose of shielding is to reduce the background count rate of a measurement system.
943 Shielding reduces background by absorbing some of the components of cosmic radiation and
944 some of the radiations emitted from material in the surroundings. Ideally, the material used for
945 shielding should itself be free of any radioactive material that might contribute to the
946 background. In practice, this is difficult to achieve as most construction materials contain at least
947 some naturally radioactive species (such as ^{40}K, members of the uranium and thorium series,
948 etc.). The thickness of the shielding material should be such that it will absorb most of the soft
949 components of cosmic radiation. This will reduce cosmic-ray background by approximately 25
950 percent. Cosmic-ray interactions in lead shields will produce lead X-rays that are in turn shielded
951 by cadmium and copper liners. Such a shield is referred to as a "graded shield." Six millimeters
952 of oxygen-free high-conductivity (OFHC) copper can also be used to reduce the cosmic-ray
953 produced lead X-rays without the cadmium liner. Shielding of beta- or gamma-ray detectors with
954 anti-coincidence systems can further reduce the cosmic-ray or Compton scattering background
955 for very low-level counting.

956 Detectors have a certain background counting rate from naturally occurring radionuclides and
957 cosmic radiation from the surroundings; and from the radioactivity in the detector itself. The
958 background counting rate will depend on the amounts of these types of radiation and on the
959 sensitivity of the detector to the radiations.

960 In alpha counting, low backgrounds are readily achieved since the short range of alpha particles
961 in most materials makes effective shielding easy. Furthermore, alpha detectors are quite
962 insensitive to the electromagnetic components of cosmic and other environmental radiation.

963 The size and interior dimensions of shields constructed for gamma-ray spectrometry or gamma
964 counting in general should be considered so that sample back scatter radiation from the shield
965 wall to the detector is minimized. In general, shield wall should be at least 10 cm from the
966 detector. Back scatter radiation will fall off as the square of the detector to shield wall distance.

967 15.9 Instrument Calibration

968 Calibrations of instruments should be made using reference materials of known and documented
969 value and stated uncertainty. These reference materials should be supplied by:

- National Institute of Science and Technology (NIST) directly;
- A standard source supplier whose measurement capabilities and/or manufacturing processes are periodically tested by NIST; and
- A user who documents derived materials with stated uncertainty and whose value has been verified with analytical and measurement systems that have been periodically tested through an unbroken chain of comparisons to the national physical standards.

Periodic testing of source manufacturers, whether they be commercial or agency suppliers or end users, is most cost effectively implemented through measurement assurance programs that are ultimately linked to NIST traceability (Hoppes, 1990).

A comprehensive discussion of germanium detector set up and calibration can be found in ANSI N42.14.

15.10 Other Considerations

15.10.1 Alpha

15.10.1.1 Troubleshooting

A number of factors can influence alpha counting results. These include attenuation or self absorption, detector contamination, and other radionuclide interference. Attenuation or self absorption corrections need not be made if constant conditions are maintained for sample and calibration standard counting. If conditions can not be held constant, then corrections will have to be made in order to produce accurate results. For example, the gamma rays from ^{137}Cs in a water matrix counted in a 90 cm^3 aluminum can will require a 15 percent correction. Individual electrical line conditioners or uninterruptible power supplies as well as supplemental air conditioning can be provided in the counting rooms to maintain electrical and environmental stability. Additionally, humidity control can also provided. Temperature and humidity may be recorded with a chart recorder.

Detector contamination can also be a problem in some cases and, therefore, detector backgrounds should be periodically checked. Contaminated detectors will have higher background counts and even when sample spectra are corrected for the presence of contamination the higher background results in higher MDAs. Finally, some alpha counters may be sensitive to beta radiation, and corrections may have to be made for this interference. For a routine operating alpha counting

system periodic instrument QC checks should be performed at some specified frequency. This would include, as appropriate, counting efficiency, background, resolution, gain, and voltage plateau.

Solid state detectors used for alpha spectrometry can become contaminated by recoil. This recoil contamination, which increases the detector background, takes place when fragments from sources travel to the detector and are implanted in the detector surface by the recoil energy imparted to the nucleus of an alpha-emitting atom. The energy of the fragments may be sufficient to implant them in the detector so that they cannot be removed non-destructively. Recoil contamination can invalidate a count after only a single sample count and cause a constant need to decontaminate equipment.

The application of a negative bias to the sample, in conjunction with an absorbing layer of air, or a thin film absorber (12 $\mu g/cm^3$) helps to keep recoil particles from imbedding themselves into the detector. For better resolution and where recoil contamination is of no concern, it is advisable to maintain a low pressure. Typically, systems can pump down to under 50 μm and, by continuously running the pump, maintain that level indefinitely.

Detector contamination dominated by two processes, alpha recoil and "volatilization" of polonium. Alpha recoil contamination occurs when an alpha-emitting nuclide on the source plate decays to an alpha-emitting daughter or string of progeny. Since the specific activity is inversely proportional to the half-life for a fixed number of atoms, recoil will produce the most background activity when relatively short-lived progeny are produced. However, if the half-lives in question are very short (say up to a few hours), they will decay away quickly enough to be of little concern in alpha spectrometry. Particularly serious are those cases that involve transfer of recoil progeny with half-lives from days to weeks, short enough that a reasonable amount of parent activity will produce a significant amount of recoil contamination, and long enough that decay back to normal background levels will require an inappropriately long time. In addition, the effect is chronic: similar recoil-producing samples counted in the same chamber will produce a long-term build-up of detector background which could eventually become serious.

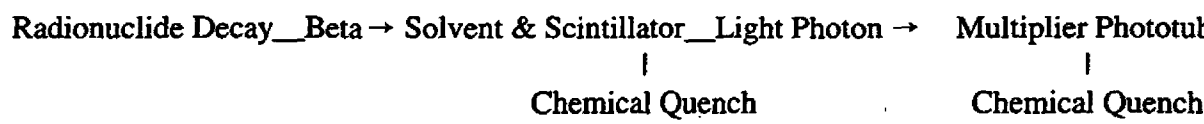
Some common examples of decay-chains that produce recoil contamination include ^{228}Th, ^{229}Th, and ^{226}Ra. It is important to realize that even β-emitting nuclides ejected by alpha recoil can contribute to alpha background if they subsequently decay to alpha emitters. For example, the direct daughter of ^{229}Th is ^{225}Ra which decays by β-emission to the a-producing daughter ^{225}Ac.

Contamination of detectors by polonium isotopes, such as ^{210}Po ($t_{½}$ = 138.4 days), should occur by some other process than alpha recoil. Note that ^{210}Po, the last radioactive member of the ^{238}U

decay series, is the daughter of ^{210}Bi, a beta-emitter. The transfer of polonium from a source to a silicon detector has been attributed to "aggregate" recoil and inherent volatilization of polonium at low pressure. Whatever the actual cause, it is clear that polonium activity is indeed transferred to detectors, a very serious problem with long-lived ^{210}Po and even worse when working with ^{209}Po ($t_{½}$ = 102 years) as a yield tracer.

Liquid Scintillation Quenching

Quenching, which is probably the most prevalent interference in liquid scintillation counting, can be defined as anything which interferes with the conversion of radionuclide decay energy to photons emitted from the sample vial, resulting in a reduction of counting efficiency. Two types of quenching may be encountered in liquid scintillation counting: optical or color quenching and chemical quenching. Color quenching results in a reduction of the scintillation intensity (as seen by the multiplier phototubes) due to absorption of the scintillation light by materials present in the scintillation solution resulting if fewer photons per quanta of particle energy and a reduction in counting efficiency. Chemical quenching results in a reduction in the scintillation intensity due to the presence of materials in the scintillation solution that interfere with the process leading to the production of light resulting in fewer photons per quanta of particle energy and a reduction in counting efficiency. The quenching process may be illustrated as follows.



One can have both types of quenching present in a sample. Note that in chemical quenching all energy radiations are equally effected, but in color quenching not all energy radiations are equally effected. Therefore, the measured sample counts should be corrected for quenching effects so that the radioactivity in the sample can be quantified. Typical quench corrections include Channels Ratio, External Standard and Internal Standardization.

Attenuation

Attenuation or self absorption corrections may be necessary for alpha counting. Attenuation corrections should be made whenever the sample matrix differs from that of the calibration standard. For example, when a gross alpha analysis is performed on an evaporated water sample of some thickness and an electroplated standard was used for the calibration. Attenuation corrections will have to be made. Alpha particle attenuation corrections will generally be necessary with a sample density thickness greater than about one mg/cm^2.

Figure 15.10 shows how severe the attenuation of alpha particles is in air.

15.10.1.2 Calibration

Alpha counting instrumentation should be calibrated with the specific radionuclide of interest or a radionuclide of similar alpha energy under the same configuration that the sample will be counted. The standard should contain the same solid material as the sample and be of the same weight. If the samples and calibration standard are not counted under identical conditions, then corrections will have to be made. Also, if there is a variation in weight from sample to sample corrections will have to be made, typically a calibration curve relating sample weight to counting efficiency is used.

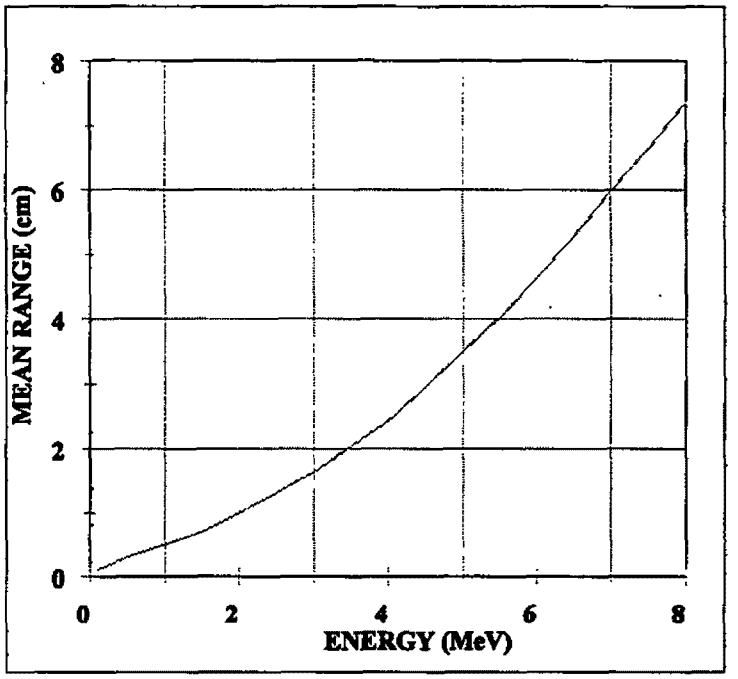


FIGURE 15.10 Range vs. Energy for Alpha Particles in Air

Alpha calibration standards are available from NIST or NIST-traceable commercial vendors. Among the radionuclides available are ^{230}Th, ^{241}Am, ^{235}U, ^{239}Pu, ^{228}Th, ^{238}U, and ^{226}Ra. Other radionuclides are also available, NIST or a commercial vendor should be contacted regarding procurement. Sources should be prepared in the manner in which the sample will be counted. The source may be procured as a solution and then prepared in the appropriate counting geometry, or the source may be procured directly in the appropriate geometry, such as an electroplated standard.

15.10.1.3 Costs

There are three major types of detectors used for alpha counting. Their cost will depend on the type of information wanted and the number of detectors in the unit.

Solid state silicon surface barrier detectors are used to count and distinguish alpha particles of different energies. An alpha spectrometer consists of a vacuum chamber, detector, electronics to amplify the signal, a multichannel analyzer, and some means of collecting data. A system with

eight detectors, vacuum pump, computer and the software necessary for data collection and data reduction costs approximately $50,000.

A liquid scintillation counter can be used to count alpha particles and in some cases provide some information about the energy distribution, although with poorer resolution than silicon surface barrier detectors. The LSC unit is typically set up to count samples sequentially, using one detector and automatic sample changer. The price depends on the background required, and will range from $25,000 to as much as $45,000. This price includes a computer and the appropriate software.

A gas-flow proportional counter is used to count samples for a gross alpha (or beta) activity. The price of a unit depends on the number of detectors, the size of each detector, and the accessories. One major accessory could be an automatic sample changer. A system with 8 to 10 small detectors (1 inch in diameter) will cost from $35,000 to more than $60,000.

There are no maintenance costs associated with an alpha spectrometer. If properly used and monitored, the system will retain its specifications for a long time. The detectors may need replacing eventually, if its resolution deteriorates or it becomes contaminated, at a cost of $500-$1,000 each.

A liquid scintillation counter requires the use of an organic scintillation cocktail, which cannot be reused. The total cost of this cocktail, combined with the cost of the sample vials, should not exceed $500 for an annual throughput of approximately 1,000 samples.

The operation expense associated with the use of a gas-flow proportional counter is for the ultra-high purity P10 gas, which is necessary if stable efficiencies and low backgrounds are required. All proportional counters should have calibrated gas regulators for accurate and reproducible settings of flow rates. The flow rate should be placed with the QC information that is with the other instrument QC. For almost constant operation of a system with eight detectors, as many as 24 tanks of P10 gas per year will be required, at a total cost of approximately $7,000.

All of the above instruments should be in a fairly constant temperature and low humidity environment, so that air conditioning and/or heating costs need to be factored in, as needed.

15.10.1.4 Quality Control

Statistical quality control (SQC) is discussed here to familiarize the reader with its application to nuclear counting instrumentation. More detailed information about SQC is provided in Chapter 19.

The primary tool for statistical quality control is the control chart. A control chart is a graphical tool for monitoring the distribution of values produced by a measurement process or system. The distribution of values observed during a period when the system is in statistical control is used to set up the control chart. Subsequent values are then plotted on the chart and inspected to ensure that the system remains in control.

Typically one ore more control charts for counting efficiency and background are maintained for each counting instrument. The instrument should be fully operational before the control charts are implemented. However, control charts should be in use before calibration of the instrument for a particular analysis to ensure that the instrument parameters are in statistical control during the calibration.

The selection of the check source for monitoring counting efficiency is critical and should be made after considering guidance in this document. The source geometry, half-life, and radiation energy are important factors.

A control chart should be based on an initial data set obtained from at least 15 measurements. Ideally, at least 10,000 counts per measurement are recommended to provide a relative counting uncertainty of no more than 1 percent. For some instruments, achieving the recommended 10,000 counts may be impractical, especially for a background control chart. It may also be undesirable to place a high-activity efficiency check source in a low-background detector because of the potential for contamination.

The initial measurements should represent the measurement system as it is used over time. Making the measurements over several days ensures that variability due to temperature and humidity changes is included. The source should be repositioned before each measurement to ensure that variability due to positioning error is included.

The mean and standard deviation of the counts or count rates are estimated from the initial data set. The mean is used as the central line (CL) of the control chart. Warning limits are placed at ±2 standard deviations from the central line, and control limits are placed at ±3 standard deviations from the central line.

Statistical tests of the data distribution should be performed at the time the warning and control limits are established. Tests for normality are common. It is also common to test whether the counts follow the Poisson model (Chapter 19).

The central line and warning and control limits for an efficiency control chart should be adjusted for radioactive decay of the check source unless the source is very long-lived. Either the limits or the data points may be decay-corrected. It may also be necessary to adjust the counting time for the check source measurements if the source decays considerably during the period when the chart is in use. It is important to note that the relative standard deviation of the measured values increases as the mean number of counts per measurement decreases.

When a measured value falls within the warning limits, the measurement system is considered to be in control. If a value falls outside the control limits, the system is considered out of control. These two rules are commonly used to evaluate control charts, although stricter evaluation criteria are sometimes used. Common sense should be exercised if the data meet the objective evaluation criteria but nevertheless demonstrate patterns or trends that might indicate developing problems. For example if a long increasing or decreasing sequence of values is observed, an investigation is probably warranted even if all of the values are between the warning limits.

Generally, if a value falls within the control limits but outside the warning limits, the system may require more attention but it is not yet considered definitely out of control. The Westgard Rules, which are recommended by ASTM E1329, provide more elaborate criteria for evaluating such measurements.

The Westgard Rules*

1. Is the measurement more than 2 sigma from the mean? If not, go to Step 7.
2. Is the measurement more than 3 sigma from the mean? If so, go to Step 8.
3. Are the last two measurements more than 2 sigma from the mean? If so, go to Step 8.
4. Is the range of the last two measurements more than 4 sigma? If so, go to Step 8.
5. Are the last four measurements more than 1 sigma from the mean? If so, go to Step 8.
6. Are the last ten measurements more on the same side of the mean? If so, go to Step 8. Otherwise, go to Step 7.
7. Accept the measurements. Stop.
8. The measurements are out of control. Stop.

*Adapted from ASTM E1329.

The following two sections on proportional counting and liquid scintillation counting are applicable to both alpha and beta measurements.

Proportional Counters

The following should be considered when QC checks are not within limits.

1. Is the standard decay corrected, correctly?

2. Check log book to see what changes were made to counter and if the repairman recently changed any switch settings.

3. If gas cylinder was changed recently, was system allowed to purge? Was correct gas (^{10}P) obtained? Verify the correct regulator pressure, and ensure the gas cylinder valve is open all the way.

4. If backgrounds are high, check for dirt or dust on the background planchet. Check window for contamination and replace if necessary.

5. Check alpha and beta voltages.

6. Check discriminator settings.

7. Check voltages on nim bin power supply (±12V, ±24V).

8. Check alpha and beta plateau voltage for drift.

Liquid Scintillation Counters

The following should be considered when QC checks are not within limits.

1. Is the standard decay corrected, correctly?

2. Has the quench value for the unquenched standard for the instrument changed? The quench value for the unquenched standard indicates the overall gain of the system. Run the autocalibration and verify the result with the historical result.

3. Check for dirt or fingerprints on outside of vial.

4. Check for dirt inside instrument.

5. Is sample two phase?

6. Has standard dark adapted and reached temperature equilibrium?

7. Check log book to see what changes were made to machine and if repairman recently changed any switch settings.

15.10.2 Beta

15.10.2.1 Introduction

Accurate beta particle measurements will depend upon the degree and extent to which the parameters that affect the measurement process under considerations are quantified. These parameters may include:

- Radiation detector used;
- Material and shape of the final sample mount;
- Form and thickness of final sample for analysis;
- Radionuclide purity of final sample;
- Final sample-to-detector distance; and
- Beta particle energy.

Beta particle attenuation or self absorption corrections to the detector efficiency may be necessary depending on the beta particle energy detection system and final sample form. The potential of detector contamination from sample measurements is a function of the type of detector used and the stability of the final sample composition. The inherent beta particle background of the various detection systems should be evaluated and its contribution removed from the sample measurement result. The beta particle measurement system should be calibrated with NIST-traceable standards and its subsequent performance held to established measurement quality requirements through the use of daily or prior-to-use quality control checks. In addition, appropriate instrument quality control should be established for background, voltage plateau, quenching, resolution and alpha-beta cross talk. Guidance on beta particle counting can be found in industry standards (ASTM D1890; D3648; E1329) and publications (NCRP Report 58; Knoll, 1989; Lapp and Andrews, 1954; Price, 1989; USPHS, 1967).

"Gross" alpha and beta counting of evaporated samples, wherein a multitude of alpha and beta-emitting radionuclides may exist, is typically used for screening of water samples. The application of such methods may be targeted for a specific radionuclide or a category of

radionuclides such as the naturally occurring nuclides or a specific radionuclide in a facility effluent. However, extreme caution should be applied to the interpretation and use of such results without a full specific radionuclide characterization of the water source under investigation. The type of analysis is to be considered "gross" and, in most cases and for a variety of sound technical reasons, the gross measurement result does not equal the sum of the radionuclides contained in the sample.

When specific radiochemistry is performed the beta-emitting radionuclide of interest will be isolated, concentrated and converted to a desired final chemical and physical form. Under these circumstances, the beta detection system should be calibrated for the radionuclide, chemical composition of the final sample form and the range of final sample weights expected from chemical recovery.

15.10.2.2 Alpha Particle Interference and Beta Energy Resolution

When properly operated or under optimal counting conditions (thin final samples or low LS quenching and high beta energy), most beta particle counting systems can separate alpha and beta particle detection events. However, the degree of alpha particle detection by the beta detector under consideration should be evaluated for each radionuclide, mixture of radionuclides or specific final sample form. Beta detection systems that are considered to have beta energy spectral resolution capabilities may be less affected by samples containing alpha-particle emitting radionuclides. However, for window gas proportional counters, alpha particle energy degradation by air, detector window or sample self absorption may lead to false beta detection without proper evaluation. A typical example would be a thick final sample matrix containing a mixture of alpha and low-energy beta-emitting nuclides.

Some commercial window gas proportional counting systems have a feature for simultaneous alpha and beta particle counting that uses a voltage pulse height discrimination for the separation of beta and alpha particle detection events. A common and more historical means of separating alpha and beta particle events is to count the sample on the alpha proportional counting voltage plateau followed by a count on the beta (plus alpha) proportional counting voltage plateau. An alpha-to-beta crosstalk factor should be determine for the final sample weight and for the alpha and beta energies under consideration. The net beta count is determined by multiplying the alpha counts (from the alpha window for simultaneous counting or on the alpha counting plateau) by the alpha-to-beta cross talk factor.

Window gas proportional counters typically are not used for beta spectrometers but instead record beta particle detection events giving rise a voltage pulse large than a discriminator setting.

Under most circumstances, liquid scintillation counters have sufficient energy resolution capability and electronic discrimination to fully separate beta and alpha particle detection events. However, due to the nature of the beta energy continuum of an emission process and the inherent resolution of a liquid scintillation spectrometer, identification and quantification of multiple nuclides contained in the same sample is complicated unless their beta energies are widely separated. Computer software and beta interference factors should be applied in such cases.

A liquid scintillation counter is typically used for Cerenkov counting. However, the final sample solution contains no scintillator as would a full liquid scintillation-sample cocktail. Cerenkov counting, due to the nature of measurement process, will not detect alpha particles of any energy or beta particles having an average beta energy less than 260 keV. Cerenkov counting is typically applied to single nuclide evaluations or for a mixture of two nuclides that have a differential maximum beta energies greater than 700 keV (e.g., ^{89}Sr and ^{90}Y). Beta interference factors should be applied in such cases.

15.10.2.3 Liquid Scintillation Quenching

The information on liquid scintillation quenching provided in Section 15.10.1.1 is applicable for beta particle detection. The degree of quenching should be determined for each radiochemical method, radionuclide or application. An appropriate correction factor/curve should be calculated and applied to the measurement results for the samples being evaluated. The magnitude of the quench correction may approach 50 percent in certain severe quenching situations.

Cerenkov counting is less sensitive to "quenching" than liquid scintillation counters using scintillation cocktails. Typically, the final sample solution is a result of a control radiochemical process that eliminates most sources of contamination, chemical impurities and variability in the final sample solution.

15.10.2.4 Beta Particle Attenuation

Beta particle attenuation should be considered for window gas proportional, plastic scintillator and solid state detector counting applications. Beta particle attenuation can result from the interaction of a beta particle with the air, detector window or the matrix atoms of the final sample. Beta particle air attenuation is a function of the distance between the sample or source and the detector's particle entrance window. Under most application for beta particle counting, this factor is typically insignificant compared to the other sources of beta particle attenuation.

Figure 15.11 shows the attenuation of beta particles is in air and water. Consideration of the detector window thickness and its beta particle attenuation becomes important when evaluating low energy beta particles such as ^{14}C. Normally, the air and detector window attenuation factors are determined as a combined beta attenuation-efficiency factor that includes the sample self absorption for a given application. In most applications, a back scatter factor for the material composition (Z value) of the final sample mount is included into a combined attenuation-backscatter-efficiency factor or, more simply, the combined detector efficiency correction factor.

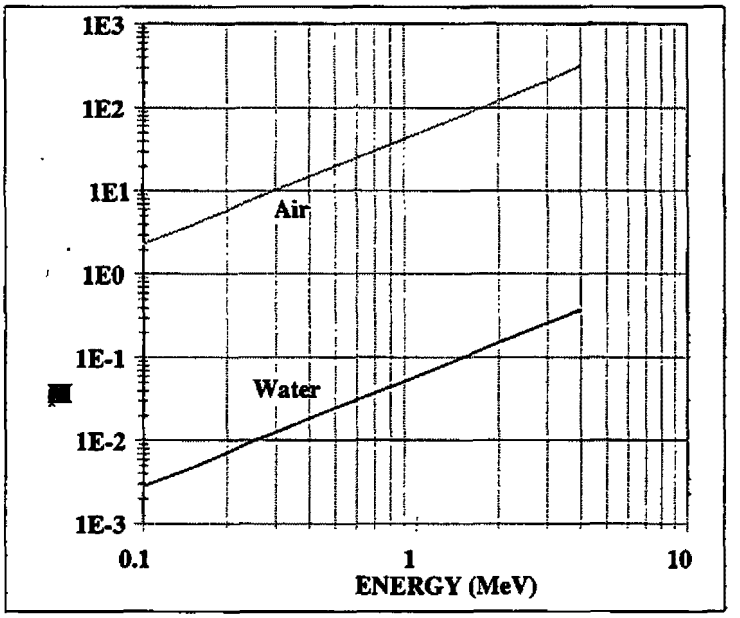


FIGURE 15.11 Range vs. Energy for Beta Particles in Air and Water

For the lower to intermediate beta particle energies, the combined detector efficiency factor is a function of beta energy, final sample mass and mass composition. For beta particles having a maximum beta energies greater than 1,500 keV, the combined detector efficiency factor is nearly constant over a final sample weight range of 0 to 5 mg/cm^2. A typical combined beta detector efficiency curve for ^{131}I (606 keV β_{max}) as CuI over a weight range of 0 to 50 mg is shown for a plastic scintillator beta detector in Figure 15.12. A complete review of the detection method can be found in reference (McCurdy et al., 1980).

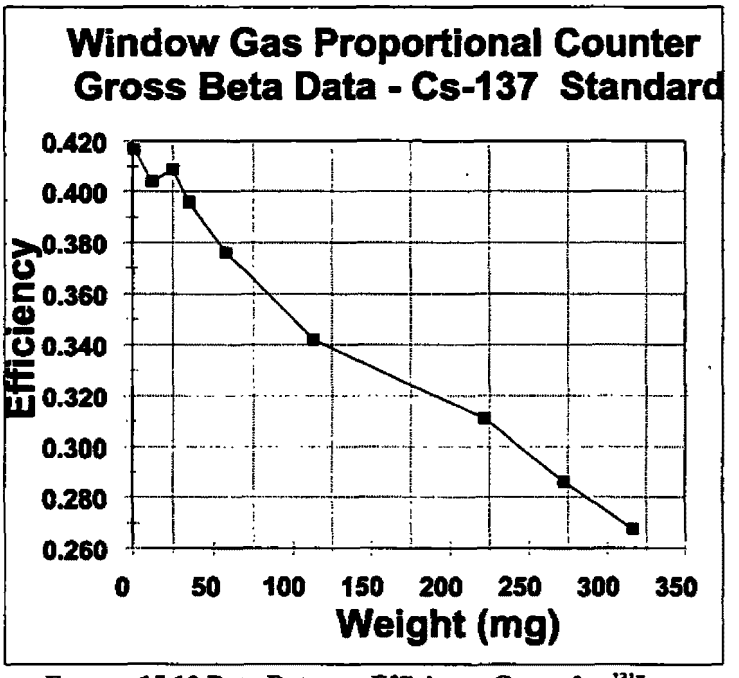


FIGURE 15.12 Beta Detector Efficiency Curve for ^{131}I vs. Weight

15.10.2.5 Calibration

Beta particle counting systems should be calibrated with the specific radionuclide under investigation or a surrogate radionuclide of similar beta energy having a comparable final sample composition and configuration. However, it should be mentioned that moderate to severe calibration biases may occur depending on the severity of the departure from the chemical composition of the final sample matrix and the beta energy of a surrogate. For this reason, the use of a surrogate radionuclide is discouraged unless the availability of the radionuclide of interest is non-existent. Corrections between the surrogate and radionuclide of interest should be determined and applied to sample results. For electroplated plated samples, a correction factor needs to be determined if the plating material of the surrogate is not the same as that used for the samples.

Cerenkov counting normally involves a single radionuclide calibration (single energy calibration) for the final sample solution. Typically, the final sample solution is a result of a control radiochemical process that eliminates most sources of variability for the calibration process.

Aqueous beta-emitting radionuclide calibration standards and sources are available from NIST or from a NIST-traceable commercial radioactive source manufacturers. The long-lived pure beta-emitting radionuclides available from NIST include: ^{3}H, ^{14}C, ^{63}Ni, ^{129}I, ^{89}Sr, ^{90}Sr, ^{99}Tc, ^{228}Ra, and ^{241}Pu. The majority of the gamma-emitting radionuclides also emit beta particles in the nuclear transformation process. Check Section 15.4 for the availability of known beta- gamma emitting radionuclides. Contact a NIST-traceable radioactive source manufacturer for the availability of other pure beta or beta/gamma-emitting radionuclides (ANSI N42.15, American National Standard Check Sources for and Verification of Liquid-Scintillation Counting Systems).

Aqueous radioactive standards can be prepared in the appropriate geometry for LS or Cerenkov counting or through chemical processing precipitated or electroplated as final sample form for counting by a gas proportional, plastic or solid state beta detection system.

15.10.2.6 Costs

There are four principal beta detection methodologies available. Window gas proportional counting and liquid scintillation counting systems (Cerenkov counting as well) can be purchased with the option of readily available automatic sequential sample counting systems. Sample capacity is typically 100. These automatic sequential counting systems are available in the $30,000 to $50,000 range depending on options. Multiple detector window gas proportional counters having a simultaneous counting capability are available from some commercial

manufacturers. The basic unit contains four detectors but several units can be combined to give eight or 16 detector systems. The basic price for such units is in the range of $20,000 to $50,000 depending on the number of detectors and options.

Solid state silicon surface barrier and ion implanted Ge or Si detectors are used to perform spectral analysis of beta emitting radionuclides. A solid state beta spectrometry system consists of a vacuum chamber, solid state detector, high voltage-preamp-amplifier instrumentation modules, a multichannel analyzer (MCA) or equivalent computerized MCA using an analog-to-digital converter and electronic data storage. Individual ion-implanted Ge detectors having an active area of 450-2,000 mm^2 and a 500 µm thickness range in price between $1,300 and $3,200. Beta resolution of these detectors is typically approximately 12 keV.0

A beta spectrometry system consisting of eight detectors with vacuum pump and computer would be approximately $30,000-$40,000, without background reducing shielding. Solid state spectrometry systems for beta particle applications, unlike that for alpha particles, would be sensitive to external background from cosmic radiation, terrestrial radiation and inherent beta radioactivity in the surrounding materials.

Automatic sample counting, plastic scintillator beta particle detection systems have not been commercialized for the radioassay laboratory setting. Most of these systems have been fabricated by the user from readily available components, electronic modules, multichannel analyzers and lead shielding. The cost of a single detector system is estimated to be less than $15,000.

Maintenance costs for the liquid scintillation counters, window gas proportional counters and alpha spectrometry systems have been discussed in Section 15.10.1.3.2 for alpha counting applications. If a laboratory already has existing units for the alpha particle measurement applications, there will be no additional maintenance cost relative to their use for beta particle measurements.

There is no maintenance cost associated with the operation of a plastic scintillator beta spectrometry system.

Costs associated with the maintenance of the room environment for the nuclear detection equipment should be considered. Service maintenance relative to the constant voltage supply or uninterruptable power sources as well as having a dust free constant temperature and humidity environment should be considered.

15.10.2.7 Quality Control

See section 15.10.1.4.

15.10.3 Gamma

15.10.3.1 Troubleshooting

Once a gamma-ray spectrometry system has been established in accordance with the manufacturer's or supplier's instructions, a daily count of a calibration or reference source should be performed to assure the system continues to operate properly. The three parameters that should be checked and recorded are: energy calibration (keV/channel), counting efficiency (count rate/decay rate), and gamma-ray peak resolution (FWHM). With the exception of a complete detector or electronic component failure (no pulses are detected at the preamp or multiplier phototube output), degradation of gamma-ray peak resolution will be the first indication that detector is not performing properly or that electronic noise has been introduced into the counting system by the preamplifier, amplifier, or multichannel analyzer. Any indications that the detector efficiency is not within statistical limits of expected values should be reported, since this value will be used to convert the observed count rate to decay rate. The energy calibration should either be recorded with sample spectral data or adjusted daily to a previously established constant value. This energy calibration should be accurately known so that nuclide identifications can be made. See page 51 for a list items to be checked if the counting system is out of specifications.

Gamma-ray spectrometry systems are extremely sensitive to both electronic and environmental conditions. Temperature changes can cause spectral shifts and improper nuclide identifications because of incorrect energy calibrations. Excessive humidity in the detector preamplifer can cause high voltage arcing which results in poor peak resolution or complete system failure. Improper pole zero settings, which effects the shape of the pulses being analyzed, can cause degradation of peak shapes and resolution. Poorly conditioned NIM power can introduce electronic noise which will also result in degraded peak resolution. Routing of cables between the detector, electronics, multichannel analyzer, computers, and monitors is very important. The introduction of any spurious electronic noise into any of the components that make up the gamma-ray spectrometry system can degrade the resulting data.

The need to make corrections for self-absorption in environmental samples during routine gamma-ray spectrometry cannot be overemphasized (Modupe et al., 1993). The correction to be made for the difference in self-absorption between calibration standards and sample matrices is usually small for intermediate and high energy photons, but it is not negligible at low energies

where the photoelectric effect is the most important mode of attenuation. The photoelectric process varies approximately as Z^{4-5} (Z is the atomic number of the elements in the medium) so that a change in the elemental composition of a sample relative to a calibration standard can require a correction factor for detector efficiency as high as a factor of 2.

$$I / I_o = \frac{1 - e^{-\mu H}}{\mu H} \tag{15.1}$$

The quantities μ and H are the linear attenuation coefficient and the thickness of sample, respectively. I_o and I are the intensities of the beam emerging from the sample container without and with an absorbing matrix in place. This is the traditional self-absorption equation. For complex counting geometries of homogeneous materials, an estimated average H (sample thickness) can be used.

The method for self-absorption correction at various energies requires that the linear attenuation coefficient, μ, of the sample matrix be known. Knowledge of μ usually requires that the elemental composition of the matrix be determined. The tedium and time required in elemental analysis may make it impractical for routine gamma-ray analyses involving large numbers of samples. Computer programs are available to calculate μ/ρ for various compounds when the percent elemental composition of the compound is known. μ/ρ is computed as a linear combination of the mass attenuation coefficients of the composite elements.

$$\mu / \rho = \sum (\mu_i / \rho_i)\ P_i \tag{15.2}$$

where P_i is the percent by weight of the ith element in the compound.

The gamma-ray path length, H, is equal to the thickness of sample. When performing gamma-ray transmission measurements to determine μ a path length of H is used. To determine the self-absorption correction for radioactive samples, the corrections are integrated for a path length of 0 to H.

When a photon beam passes through a homogenous sample of mass attenuation coefficient, μ/ρ, density, ρ, and thickness, H, the percentage beam attenuation, A, is given by

$$A = \frac{I_o - I}{I_o} 100\% = (1 - e^{-(\mu/\rho) H \rho}) 100\% \tag{15.3}$$

15.10.3.2 Calibration

Most gamma-ray spectrometry systems are calibrated with either single or mixed standards in an exact matrix and geometric form as the samples to be analyzed. However, there are computer codes that can calculate detector efficiency from the physical dimensions of the detector and sample counting geometry (Mitchell, 1986 and 1988, Hensley et al., 1997). Commercial standards of single or mixed gamma-ray emitters in a matrix of known chemical composition and density can be prepared in user supplied containers. Calibrations based upon these standards can then be adjusted to correct for any differences in composition and density between the calibration source and the sample (Modupe et al., 1993).

Table 15.2 lists some gamma-ray emitting nuclides that can be used for energy and efficiency calibration (Sanderson et al., 1993; Browne et al., 1986).

TABLE 15.2 Nuclides for Gamma-ray Spectrometer Calibration

NUCLIDE	ENERGY (KeV)	HALF-LIFE
^{210}Pb	46.5	22.3 years
^{241}Am	59.5	432.2 years
^{109}Cd	88.0	462.6 days
^{57}Co	122.1	273 days
^{141}Ce	145.4	32.5 days
^{139}Ce	165.9	137.7 days
^{203}Hg	279.2	46.6 days
^{51}Cr	320.1	27.7 days
^{113}Sn	391.7	115.1 days
^{85}Sr	514.0	64.8 days
^{137}Cs	661.7	30.0 years
^{54}Mn	834.8	312.5 days
^{88}Y	898.1, 1836.1	106.6 days
^{65}Zn	1115.5	243.8 days
^{60}Co	1173.2, 1332.5	5.27 years
^{40}K	1460.8	1.28×10^9 years

15.10.3.3 Software

Most laboratories are now using commercially available software for the analysis of gamma-ray spectra. These programs are easy to use and do not require the user to be an expert in gamma-ray spectrometry. An evaluation of some of these programs in 1987 indicated there were substantial differences in the abilities of the programs to resolve multiplets of unequal intensity and to analyze complex spectra (Sanderson 1988). Another evaluation was completed in 1992 (Decker and Sanderson, 1992) since many of the programs had undergone numerous revisions and there were a few new programs available. The second evaluation indicated a substantial improvement in the deconvolution of doublets and the results of the analysis of a Chernobyl air filter were much more consistent than when a similar filter was analyzed in the first evaluation. The six programs analyzed in 1991 include GAMMA-W from Germany, INTERGAMMA from France, OSQ/Plus from Canada, SAMP090 from Finland (supplied by Canberra Industries, USA) and OMNIGAM and GDR from the United States. Some of the features which contribute to a good program included the ability to display the spectrum as well as calculated calibration files, the ability to manually insert peaks during the fitting procedure, an extensive nuclide library and the ability to easily transfer nuclides to smaller, working libraries, an analysis report which includes the names of the calibration files used, a peak fit report including any problems with the shape of the peaks, and identification of the peaks used in the activity calculation as well as any problems with interfering lines.

In 1996 the Environmental Measurements Laboratory of the U. S. Department of Energy began a Gamma Spectra Data Evaluation program (Decker et al., 1996) whose goal was to test the ability of the present day software to accurately identify and quantify the nuclides in a complex spectra and the ability of the user to properly utilize the software. In order to do this, synthetic spectra were generated using the computer code SYNTH developed by Walt Hensley at the Pacific Northwest National Laboratory. The spectra were then converted to a variety of formats on disk and Digital Equipment Corporation (DEC) TK 50 tape and sent to DOE laboratories and DOE contractors. A calibration spectrum, a background spectrum and three sample spectra were sent to each participant. These spectra simulated those that would be obtained when an air filter was counted 10 cm from a 22 percent coaxial detector with a 0.5 mm beryllium window. Two of the samples contained fallout and naturally occurring nuclides with half lives greater than thirty days. The third sample contained both short and long lived fission product nuclides. Thirty one laboratories participated using 16 different software packages. The software packages included Aptec, Vertechs GDR/P, Nuclear Data ASAP, various Ortec packages, and various Canberra packages for both the PC and the DEC MicroVax. Most of the laboratories did fairly well with the first two samples. A few laboratories reported nuclides that were not present in the third sample and did not accurately quantify those that were. The results did not seem to be software

dependent but were due to the user utilizing or not utilizing available software features properly. There was quite a wide range of numbers for both the uncertainty terms and for the minimum detectable activities which seems to indicate we need a consistent way of calculating these terms to make them more meaningful.

15.10.3.4 Costs

Gamma-ray spectrometry systems can cost from $14,000 to well over $60,000 depending upon the choice of detector. For a 75 x 75 mm NaI(Tl) system the costs would be approximately $1,000 for the detector, $5,000 for a 10 cm graded lead shield, and $8,000 to $10,000 for a multichannel analyzer. Very large HPGe detectors will cost more than $50,000. The actual detector cost will depending upon the size of the germanium crystal, its resolution, and method of cooling. Data reduction costs (software and computer) would be an additional expense for either type of system.

NaI(Tl) detector systems do not require any additional maintenance beyond what any laboratory electronic system requires. Each HPGe detector will require approximately $1,200 per year for liquid nitrogen to maintain their operating temperature. An electrical/mechanical cooler can be used in place of a liquid nitrogen cryostat but it will require 0.5 to 1.0 kW of power around the clock to operate. Both systems should be operated at constant temperature for reliable performance. This may require substantial air conditioning.

15.10.3.5 Quality Control

Initial data to prepare solid state gamma detector QC charts may be obtained by counting a mixed gamma point source between 20 to 30 times (Ideally, these counts should be over a period of several weeks. However, if time does not permit, the counts may be accumulated over 1 to 7 days.) Two or three QC charts (depending on age of mixed gamma point source) are initially established for the mixed gamma point source and control limits are established for background. The three source charts cover the low energy (88 keV, ^{109}Cd), the medium energy (661.6 keV, ^{137}Cs), and the high energy (1,332.5 keV, ^{60}Co). The source is counted until between 10,000 to 40,000 counts are obtained in each photopeak.

Background QC charts are established according to the procedure already listed for Proportional and liquid scintillation counters with the following exception: the background is counted and the total counts in the spectrum are obtained by summing the counts in the entire spectrum.

The resolution of the detector (FWHM) is measured each month and recorded, but it is not plotted. A NIST ^{60}Co source is positioned 25 centimeters from the end-cap face and counted for 100 minutes. The FWHM is calculated by the peak search program for the 1,173.2 keV and 1,332.5 keV peaks, and recorded in the logbook.

When the energy of the source QC exceeds the specified energy tolerance (for example ±0.75 keV) from its initial calibrated value, the analyzer system should be recalibrated. First determine whether a gain or zero shift has occurred. A gain shift is a nonlinear shift in channels of low and high energy peaks (i.e., ^{109}Cd peak shifts ±l channel and ^{60}Co peak shifts ±3 channels). A zero shift is a linear shift in channels for both low and high energy peaks (ie., ^{109}Cd peak shifts ±l channel and ^{60}Co shifts ±l channel also). Make the appropriate adjustments to the amplifier (gain) or the Analog to Digital Converter (zero). Recalibrate the analyzer and record the slope (keV/channel) and the zero intercept in the log book. If the best fit of the recalibration curve is a nonlinear fit (quadratic), record the "Q" coefficient, keV/channel^2, in the log book. Also record the updated FWHM calibration factors, slope, offset, and FWHM at 1,332.5 keV in the log book.

The following should be considered when QC checks are not within limits.

- Is standard decay corrected to the proper date?
- Check sample positioning.
- Check for zero shift.
- Check for gain shift.
- Check full width at half-maximum.
- Check nim bin power supply voltages (±6 V, ±l2 V, ±24 V).
- Check efficiency tables.
- Check for moisture on the detector due to recently filling the dewar with liquid N_2.

15.10.4 Non-Nuclear Instrumentation

15.10.4.1 ICP-Mass Spectrometry

ICP-MS is one of the most versatile and sensitive atomic spectroscopy techniques available. It can be used to determine the concentrations of over 70 elements. The detection limit of the technique extends down to the parts-per-billion range in soils and to the parts-per-trillion range in waters. This sensitivity makes ICP-MS an attractive complement to decay-counting techniques in the radiochemical analysis laboratory. For very long-lived radioisotopes (those with half-lives over 10,000 years, e.g., ^{244}Pu, ^{99}Tc, ^{129}I), ICP-MS may be faster and more sensitive than decay counting. In addition, sample preparation for ICP-MS can avoid some of the analyte separation

and purification steps required for decay counting, providing an additional dimension of time savings. Another important feature of ICP-MS is its ability to provide isotopic distribution information (e.g., ^{238}U vs. ^{235}U). This information is frequently useful in determining the age and/or origin of materials. (ASTM C758, C759, C799)

The isotopic discrimination capabilities of ICP-MS make possible the calibration technique known as isotope dilution. In this procedure, a sample is analyzed for one isotope after having been spiked with a different isotope of the same element (e.g., analysis of ^{235}U might involve spiking with ^{233}U). The spiked sample is carried through all preparation and analysis steps; in this way, any matrix or procedural effects that might influence the ^{235}U signal will influence the ^{234}U signal to precisely the same extent. Final quantization relies on measuring the ratio of unknown (here the ^{235}U signal) to the known (^{234}U) signal. Isotope dilution is a way of generating highly precise and accurate data from a mass spectrometer and has been used in the characterization of many certified reference materials.

Although an ICP-MS instrument is extremely delicate, with proper care and preventive maintenance system up time should range between 80 to 95 percent. An initial investment of about $200,000 will be required to obtain a current commercial state-of-the-art system. Annual maintenance costs will run from $5,000 to $20,000 depending on the purchase of a service contract.

For more sophisticated measurements, at substantially higher cost, an ICP-MS with magnetic sector, instead of quadrupole, detection can be applied. Sector instruments are capable of resolving species of very similar mass. For example, ^{99}Tc might be resolved from a contamination of ^{99}Ru with a high-resolution mass spectrometric detector. More typically, high resolution instruments are employed for their higher signal/noise ratio, and therefore superior detection limits. A single-collector high-resolution ICP-MS can be purchased for roughly twice the cost of a quadrupole ICP-MS, or about $300,000. For enhanced sample throughput a multiple-collector instrument might be purchased for about $500,000. These instruments, like most analytical equipment, can be expected to require about 2 to10 percent of their purchase costs in annual maintenance costs.

Thermal ionization mass spectrometers are available at a cost of $500,000. These instruments rely not on a plasma for ionization, but rather for thermal ionization from a heated filament. They provide more precise measurements than routine quadrupole ICP-MS but require substantially more delicate operator involvement, leading to markedly reduced sample throughput.

Time-of-flight plasma mass spectrometers have just recently appeared on the market; they have not yet built up a historical record of performance that would permit reliable comparison with the ICP-MS equipment described above. Likewise, Fourier-transform mass spectrometers are still in the research phase and cannot yet be considered practical options for routine radiochemical analysis.

15.10.4.2 Laser

APPLICATION

Lasers can be used to excite uranium (ASTM D5174) and lanthanide complexes in solution. During or following excitation, the complex relaxes to a lower energy state by emitting photons of light that can be detected. The amount of light produced is proportional to the uranium or lanthanide element concentration.

The light emitted can be detected by fluorescence or phosphorescence. With fluorescence and phosphorescence, the detector is at right angles to Laser excitation. Fluorescence light is emitted simultaneous to the excitation.

Phosphorescence detecting differs from fluorescence in that the light emitted is not simultaneous to the excitation. This enables the light source to be pulsed and the measurement to occur when the Laser source is off. This provides improved signal to noise over fluorescence. The light signal from organic material will decay promptly, since they have a short relatively lifetime, and not be available to the detector which is gated off at this initial time. A pulsed nitrogen dye Laser can be used as the source. Other Lasers can also be used. Chloride ion and other ions may cause interferences and may need to be removed before measurement.

Kinetic phosphorimetry measures the rate of decay of the uranium or lanthanide element complex signal. Measurements are taken at fixed time intervals. In aqueous solution, the uranium or the lanthanide element is complexed to reduce quenching and increase the lifetime of the complex.

UP/DOWN TIME

Some reagents may have relatively short shelf life and need to be ordered accordingly. The life of a plasma cartridge is one to three years.

1638 COST

1639 The initial cost is about $34,500 with a computer and $53,500 with an automatic sample changer.
1640 The cost of replacing a plasma cartridge is $1,400.00. The cartridge lifetime is 1 to 3 years
1641 depending on usage.

1642 15.10.4.3 Radionuclides Analyzed By Neutron Activation

1643 TECHNETIUM-99

1644 Neutron activation analysis methods have been employed since 1972 (Foti et al. 1972a; 1972b).
1645 The method was developed and applied for the analysis of ^{99}Tc in mixed fission products (Bate,
1646 1979).

1647 The method employs chemical separation of ^{99}Tc from most fission products by a cyclohexanone
1648 extraction from a basic carbonate solution. ^{99}Tc is stripped into water by addition of CCl_4 to the
1649 cyclohexanone phase and then adsorbed on an anion exchange column in a concentrated form.
1650 Neutron irradiation of the isolated ^{99}Tc could be made in the pneumatic facility at a high flux
1651 isotope reactor (e.g., at a flux of $5x10^{14}$ ng/cm^2/sec for approximately 11 seconds. Thus, after
1652 irradiation ^{99}Tc is induced to ^{100}Tc, which, because of its 15.8 second half-life, requires an
1653 automatic process to measure its 540 and 591 keV gamma lines.

1654 The lower limit of detection of the analysis under these conditions is approximately 5 ng and
1655 samples up to 100 mL volume can be processed. The method has been applied successfully to
1656 reactor fuel solutions and off-gas traps containing $6.5x10^{-4}$ to 240 µg ^{99}Tc/mL.

1657 IODINE-129

1658 Iodine-129 can be determined by neutron activation and subsequent measurement of the
1659 12.4 hour ^{130}I produced by the neutron capture reaction. The method (Bate and Stokely, 1982)
1660 utilizes conventional I valence adjustments and solvent extraction to isolate the I fraction.
1661 Chemically separated ^{129}I is adsorbed on an anion exchange resin before being loaded for
1662 irradiation. With a neutron flux of $5x10^{14}$ ng/cm^2/s for 100 seconds a lower limit of detection of
1663 0.03 ng can be achieved.

1664 ^{129}I also can be determined directly by mass spectrometry (Strebin et al., 1988). The measurement
1665 limit by this technique is approximately 2 femtograms.

Special counting techniques have also been applied to the analysis of ^{129}I. Figure 15.13 shows an efficiency plot using beta-gamma coincidence counting.

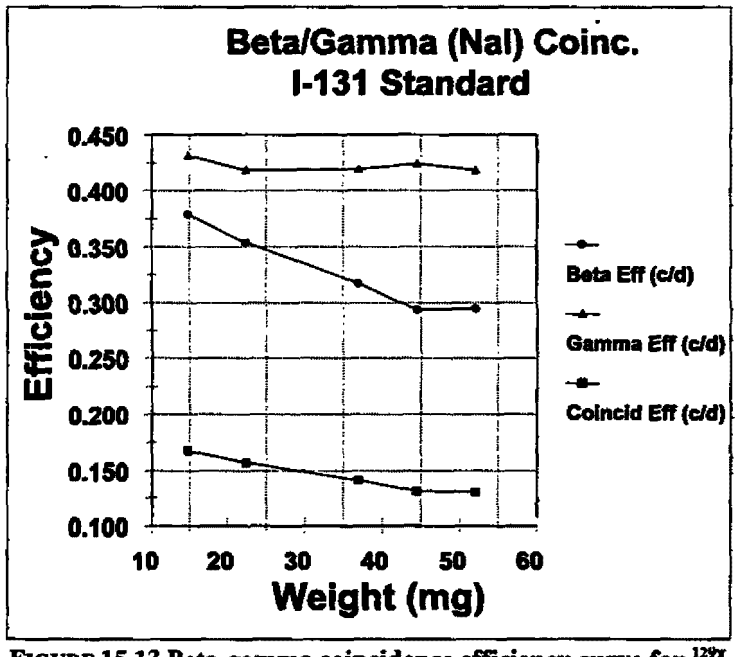


FIGURE 15.13 Beta-gamma coincidence efficiency curve for ^{129}I

URANIUM, THORIUM, AND PLUTONIUM

Neutron Activation analysis method was employed to determine uranium in the hydrogeochemical samples from Savannah River Plants within the scope of the National Uranium Resource Evaluation Program sponsored by DOE. Uranium was determined by cyclic activation and delayed neutron counting of the ^{235}U fission products. The method relied on the absolute activation techniques using the Savannah River Reactor Activation Facility.

Neutron Activation Analysis followed by delayed-neutron detection was commonly used for determination of ^{235}U, ^{239}Pu, and ^{232}Th (Echo and Turk, 1957; Hochel, 1979; Alfassi, 1990).

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ATTACHMENT 15A FIELD MEASUREMENTS

15A.1 Introduction

The scope of environmental remediation work taking place across the country in the public and private sector has led to a need to improve the speed and cost-effectiveness of measurements for characterizing contaminant levels at sites and assessing the results of cleanup efforts. In particular, the time for decisions that are required during soil excavation and waste segregation should be kept short to avoid delays that tend to increase labor costs. Thus, the time it takes to collect, prepare and analyze samples can be a limiting factor. To this end, one can use mobile laboratories at the field site to reduce sample handling and transit times. However, even with these, the sheer volume of samples can overwhelm processing and analytical capacity. Therefore, measurements performed directly in the field (in situ) that do not require the collection and processing of a sample are an attractive alternative. Fundamentally, a field measurement gives the concentration of a contaminant at the same place where one might otherwise have collected a sample. In effect, the instrument is brought to the sample rather than the sample to the instrument. Frequently, the field measurement can be performed within minutes with a result obtained in what is essentially "real time."

15A.2 Analytical Level of Measurements

Over the years, field measurements have formed an important component of standard radiological surveys. Typically, these measurements have comprised scans for gross levels of alpha or beta/gamma radiation. These types of measurements, particularly where judgment is used to evaluate a change in an instrument or audible signal, are semi-quantitative in nature and therefore would be designated at analytical level 1 under the EPA classification system used in the past or Analytical Support Laboratory(ASL) level A of the American National Standards Institute (ANSI). These levels reflect the fact that the measurement is intended for screening purposes.

However, field measurements can be performed at a higher analytical level. For example, an exposure rate measurement using a pressurized ionization chamber (PIC) is definitive for assessing the external dose rate from penetrating (gamma) radiation. In this situation, the PIC provides a direct reading of the desired measurement quantity at the actual point of interest.

Another example of a field measurement technique that has been used successfully since the 1960s is in situ gamma-ray spectrometry (ICRU, 1994). This technique provides radionuclide-specific information. In its simplest application, a spectrometer could be used to identify characteristic peaks in the energy spectrum that would point to the presence of a particular radionuclide at the measurement location. On a semi-quantitative basis, *in situ* spectrometry could serve as screening technique where the relative count rates—in particular spectrum peaks—are compared among measurement locations. At a higher analytical level, an appropriate calibration can be performed so that a spectrometer could be used to determine the radionuclide concentration in the media under study. Since this represents a contaminant-specific measurement where particular QA/QC checks can be made, it would be classified traditionally at the data quality objectives (DQO) analytical level 2, or ASL B.

Despite a number of successful applications of *in situ* spectrometry over the years, issues have arisen regarding the level of data quality that is obtained with this or any other field measurement technique for the purposes of demonstrating RCRA, CERCLA, and other regulatory compliance. In the past, field measurements by definition have not been considered to possess the quality control that needs to be established at a DQO analytical level of 4 (analogous to ASL D) in the laboratory. However, the distinction between screening level and higher level measurements is based on factors relating to data quality, which should be demonstrable. In principle, the rigorous QA/QC protocols and documentation required for analytical level 4, using EPA Contract Laboratory Program (CLP) procedures, or ANSI ASL D, could be applied to radionuclide-specific field measurements. Using field techniques at a higher analytical level is also in keeping with the latest EPA proposals for performance based measurement systems.

Typically, a projection of cost or time savings using a novel field method leads to its substitution for a more standard sampling/laboratory analysis method. In doing so, the intended applications of the field measurement method need to be established clearly. Using the DQO process, the requisite analytical level can be determined for the data that are to be collected. This analytical level should then be demonstrated through an objective judgement process whereby the data quality indicators are critically examined. Included would be those that arise when applying the DQO process (the "PARCC" parameters: precision, accuracy, representativeness, completeness, and comparability). Other related indicators or elements which can be broken out separately and which need to be addressed include documentation, instrument operating conditions, site conditions, interferences, limitations, calibration procedures, minimum detectable concentrations, reference measurements, record keeping, quality improvement, and management assessment. The following sections will provide some discussion on each of these elements as they apply to field measurement data quality level. Although the discussion is based on experiences with in situ spectrometry, the elements would generally apply to other field measurement techniques as well.

It would be expected that a demonstration of the data quality level of a field technique be performed in concert with regulatory bodies and stakeholders to obtain acceptance.

15A.3 Documentation of Methodology

A field measurement technique, like its counterpart in the laboratory, requires thorough documentation including the description of apparatus and materials, specification of personnel training/qualification level, listing of quality control checks, review of safety considerations, and issuance of non-conformance reports when necessary.

Training materials, equipment manuals, reference texts, articles from technical journals, and laboratory reports are all potential sources of background information for describing a method. It would be expected that information be extracted from these sources and a comprehensive report issued that provides the necessary background and specifics for a particular site and application. This would essentially take the form of a written procedure. For multiple applications across a site, further detail may have to be provided in project-specific plans, as the conditions under which a technique is used may vary among areas. The guidance and recommendations given by standards groups can also form a key part of documentation. Adherence to these standard procedures allows one to proceed with some confidence in the measurements process. It is expected that standards groups will increasingly devote their efforts to field measurements techniques in the future.

Individuals who will be working with the instruments and data collected need to be qualified. Educational backgrounds and necessary experience should be determined and appropriate training given for each area of work. Training and procedure manuals need to track revisions that invariably result as measurement programs progress.

Quality systems documents would include a general site-wide quality plan with specific factors like performance tests, pre- and post-operational checks, frequency of calibrations, and replicate measurements addressed in a separate method-specific quality systems section or document. Quality systems includes documenting procurement specifications for apparatus and control of materials and services such as calibration sources. Also, the turnaround time for field measurements may be important to specify not only for cost and schedule control but for limiting the time lag between measurements under changing environmental conditions.

Unforseen measurement conditions and unusual equipment malfunctions will lead to situations where doubt is cast on the validity of a field measurement. Tracking these failures will help to elucidate the problems over time and a provide a basis for corrective actions and modifications to

the procedures for future measurements. Situations where obvious bad data is collected despite the fulfillment of QC elements will require the writing and issuance of a non-conformance report with subsequent root cause analysis.

15A.4 Instrument Operating Conditions

Specification of instrument operating conditions is fundamental in the field as in the laboratory. These would include power and cooling requirements as well as an acceptable range in temperature and humidity conditions. The physical set-up of the instrument, such as a reproducible sample-detector geometry, also should be specified. For laboratory radioactivity counting systems, it is generally a planchet, can, bottle or similar small volume where the distribution of activity within the sample volume is assumed to be homogeneous. For a field measurement, the sample is in a form such as an area of ground, a storage drum, or wall. Distances and orientation to the measured area or object need to be specified and held within control limits.

For a field measurement, the distribution of activity within the volume of measurement should be considered, since one does not usually have the luxury of mechanical blending as in the case of a laboratory sample. The field of view of the detector with respect to lateral and depth displacement within the volume under measurement needs to be established. For large volume sources, this generally means determining the response of the instrument across all angles or radiation incidence, not just the front face. While one cannot necessarily control the distribution of a contaminant, the instrument response needs to be established so that the integrated signal that it measures can be converted into a meaningful average result over the volume measured and the sensitivity to non-homogeneous activity distributions determined.

15A.5 Site Conditions/Limitations

Preparing a site for a field measurement is analogous to preparing a sample for analysis. Procedures need to be followed that will assure that the measurement will yield a valid result. This might include removing obstructions and accounting for topography and ground cover such as vegetation or surface water. The radiation absorption properties of the type of soil where measurements are made may have to be determined beforehand depending upon the energy and type of radiation being measured.

A significant element which should be addressed in performing field measurements is changes in the "sample," i.e., changes in the field conditions at the measurement point. For example, measurements at the same location several days apart may be not be comparable if soil moisture

conditions have changed. Precipitation events would increase soil moisture, while hot, dry conditions would lead to a decrease in soil moisture.

Depending upon the instrumentation and the physical basis of the measurement, the effects of such variables as air and soil temperature, humidity, air pressure or related meteorological parameters may have to be taken into account.

Limitations should be specified for a field measurement technique. They could include site conditions such as the water content of soil, the degree and type of ground cover, the size of an area, and the estimated depth of contamination. The radionuclide mix and the concentration level could also be limiting factors.

15A.6 Interferences

The effects of interferences need to be assessed for proper QC in a field measurement. As compared to a laboratory setting where there is generally a controlled environment, adverse instrument effects may result from extraneous signals or electronic noise that could be produced by power line or other electromagnetic interference. Interferences in a measurement could also result from personnel—whether instrument operators or other workers—who enter into a measurement area and attenuate the measured radiation.

Whereas a laboratory counting system may employ a shield to block out background radiation, a field measurement system is exposed to ambient radiation. If significant direct or scattered (shine) radiation is present from extraneous sources, collimation or shadow shielding may be necessary. In high radiation fields, the effects of ionization in electronic components may present a problem. In this case the sensor assembly could be kept at the measurement point with the signal processing and other electronics kept at a distance.

As in the case of laboratory analysis, attention should be given to the mix of radionuclides that may be present. Interferences can result from the inability to resolve the primary energies emitted by the nuclides or because there is a high amount of secondary (scattered) radiation present.

15A.7 Calibration

Calibration requires that the instrument response to a known level of measured substance be determined. This generally takes the form of measuring standard reference materials or samples spiked with known quantities.

Direct calibrations using standards or spikes are usually applied to laboratory-based counting systems since only small quantities are needed for the sample volumes used. For field measurements, direct calibrations using large volume sources with a known concentration can be performed as well, although this is generally impractical and potentially expensive. In place of this, a field calibration factor for a particular source geometry and matrix composition can be derived using a two-step process. This entails determining the response to incident radiation (fluence) as a function of energy and angle (by experimental and/or theoretical means) and then calculating the fluence at the point of measurement from a given source geometry and matrix. Two-step calibration methods sometimes are applied to laboratory sample counting geometries as well.

Although a two-step process may be used for field calibrations, traceability still can exist insofar as certified point or other sources can be used in the calibration process. The calibration factor may actually represent an integrated response to a collection of sources or a single source at many different positions. In the case of a spectrometer, calibration points will need to be spaced out across the energy range of interest. Depending upon saturation effects, the calibration may also have to extend across a range in concentrations to assess the effects of signal processing dead time and pulse pile-up.

15A.8 Minimum Detectable Concentrations

Standard to any high quality measurement technique and integral to the DQO process is an a priori estimate of the detection limits of the measurement system. This needs to be done for a field measurement technique, although it may be necessary to first obtain preliminary readings in the area where measurements are to be performed. For example, the minimum detectable concentration (MDC) for a particular radionuclide will be affected by the continuum of scattered radiation present in a spectrum from other radionuclides in the soil or from sources of scattered radiation outside the area under investigation.

In some situations the sensitivity for a given count time can actually be higher for a field measurement as compared to a laboratory-based sample measurement, thus producing a lower MDC. This will result when the field detector gives a higher count rate per unit concentration because there is a far larger sample being analyzed.

15A.9 Precision

The precision of field measurements is determined with replicate measurements as in the case of laboratory measurements. To avoid potential changes in field conditions, replicate measurements can be performed sequentially with minimum time lag.

In many cases, a field measurement is a non-destructive technique. Thus, replicate measurements are easily performed. Using the results from a successive set of measurements (5 to 10), a standard deviation about the mean can be calculated. This can then be compared to the counting error for a single measurement that is based on Poisson statistics to assess precision.

Rather than perform many replicate measurements at one point, it can be more instructive to perform two or more measurements at several different points. The reproducibility can thus be judged for a variety of site conditions.

15A.10 Accuracy

Estimates of accuracy for a field measurement can be obtained through uncertainty propagation just as in the laboratory. Factors to consider include potential bias due to uncertainties in the calibration source, variations in the assumed sample/detector geometry, uncertainties in the sample matrix composition, environmental conditions, as well as the statistical counting error.

Overall system accuracy can be checked with comparisons to other techniques, or to results from an independent organization using the same technique.

15A.11 Representativeness

Representativeness refers to the degree to which a measurement reflects the condition at a location or whether a group of measurements reflects the conditions in a particular area. Generally, one desires that measurements (or samples) provide a value of a radionuclide concentration that in turn yields the best dose estimate (and thus risk) to a member of a critical group for a particular scenario. In order to achieve representativeness, a number of samples or measurements in a given area would be required in order to achieve a given confidence level or power using a statistical test.

Representativeness is affected by the heterogeneity of the contaminants in the media under investigation. Perhaps more than any other factor, field and laboratory measurements may differ at any particular measurement location due to the effects of heterogeneity. Heterogeneity can

exist in both the lateral and depth distribution of a contaminant and can take the form of changes in concentration across various distances: a centimeter or less, as would result from hot particles; meters, as might occur from dumping and localized spills; and tens or hundreds of meters, as from up-wind airborne sources. Survey designs incorporate techniques and sample/measurement densities to accommodate these variations. The number of measurements and the standard deviation about the mean are fundamental parameters to judge whether the mean concentration that is measured is within a certain confidence limit. These parameters can be used to compute the t statistic or applied to other statistical tests.

Where variations in concentration occur on a scale of tens of meters or more, it can be expected that either field measurements or soil sampling will give similar results. It is where the variations on the scale of a few meters or less occur that agreement between any particular pair of field measurement and soil sample results might suffer. However, if the mean concentration in an area should be determined, a sufficient number of measurements or samples can ultimately yield the same average result, regardless of where the measurements or samples are taken within the area under investigation.

Depending upon the objectives of a measurement program, a field method could inherently have an advantage over discrete sampling. If the viewing area of a field instrument is significantly larger than the area of a soil sample, a set of field measurement results would tend to show a smaller standard deviation as compared to a set of soil sample data in a heterogeneous area. The mean obtained for a given number of measurements would then be more representative of the true mean. A wide measurement area represented by a field method could also be consistent with the assumptions of a dose model which averages over a large area.

15A.12 Completeness

Measurement losses can occur in the field just as sample losses can occur in the lab. They result from equipment failure, improper measurement procedures, or environmental factors beyond the control of operators. Survey designs should incorporate allowances for sample losses by specifying the collection of more than just the minimum number of samples needed to support a decision.

There is somewhat of an advantage for a field technique in that QC checks can be performed at the time of the measurement. Problems can then be immediately identified and the data rejected on the spot. Another measurement can then be performed in place of the lost measurement.

15A.13 Comparability

Comparability is a critical factor that readily establishes the validity of a field technique. It can be established by performing a study in which field measurement results are compared to those given by an independent technique, such as sampling and laboratory analysis. In some situations, it may be possible to compare two different field techniques.

In performing a direct comparison study, it is important to establish that the two techniques are measuring the same thing. For instance, a technique that measures a contaminant concentration in the surface soil may compare poorly to one that is integrating down to greater depths. This situation would result where there is a non-uniform concentration depth profile of the contaminant. Where comparisons are made to soil samples, core depths can be adjusted to better match the effective viewing depth of the field measurement. The lateral distribution of the contaminant concentration across the ground could also be a factor. In this situation, compositing samples may be required to yield a better average with which to compare a field technique.

Other factors to consider for data comparability include the soil moisture and stone content of soil. Where contaminant concentrations are determined with a field technique, the value is based on the wet weight of the soil in contrast to laboratory analysis which is performed on a dry weight basis. Corrections to one of the data sets therefore need to be applied. Similarly, one should consider the effects of soil sample preparation where large stones are screened out. The concentration which is then determined is based on the activity associated with the finer particle content of the soil. If there is little or no activity in the coarser fraction, a concentration for a soil sample would be higher than that given by a field technique which has averaged in the stone content.

In place of comparing single field measurement points to single or composited samples, one can instead compare the averages of sets of field measurements to sets of soil samples over a particular size area. This would be useful to establish comparability where there is a known heterogenous distribution of the contaminant and the techniques under comparison are measuring very different areas of soil.

15A.14 Reference Measurements

An important QC practice in the laboratory involves the regular analysis of reference materials to confirm system calibration and performance. In practice, an analogous check can be performed for measurements in the field. A reference measurement location at a site can be designated as a field quality control station where routine, perhaps daily, measurements of the contaminants of

concern are performed. QC charts can be kept which show the results of these measurements and control limits can be specified accordingly. Unusual trends can then be identified early and corrective actions taken before unusable data is generated. Measurements at a station such as this also serve to demonstrate the effects of environmental variables such as temperature and humidity.

To further qualify a field station, intensive sampling can be performed with laboratory analyses to determine contaminant concentrations. In this situation, relatively homogeneous conditions (soil type, contaminant concentration) would make the comparison more favorable and help to trace any bias between measurement methods that might be observed.

In addition to reference materials, the analysis of blanks is a regular feature of laboratory-based counting systems. This establishes that contamination of equipment and materials has not occurred. Similar contamination can occur to field instrumentation such as wind blown soil particles in crevices, encrusted mud on the underside of equipment, or soil plugs in tripod legs. For a field measurement technique, it may be possible to check self-contamination by performing measurements in a background area where the contaminant in the soil is essentially zero. If the contaminant is present in background, such as ^{137}Cs from nuclear weapons fallout, an offsite area at least can serve to establish a regional baseline measurement. As a standard measure of precaution, routine scanning of equipment can be performed with friskers, especially after work in highly contaminated areas.

15A.15 Record Keeping

Field personnel need to use log sheets or books to record necessary information about the site conditions, measurement parameters, and data storage. In place of chain of custody forms for samples, analogous records may be required for data printouts or electronic files of results (spectral data) obtained in the field as they pass through different levels in the organization (data entry, data analysis, validation, etc.).

Maintenance logs or files on specific pieces of equipment need to be kept. Factory repairs or in-house replacement of components should be noted as any changes to an instrument are likely to require recalibration. Equipment and component failures should also be tracked.

15A.16 Quality Improvement

Operating experience generally leads to fuller knowledge of instrument performance and characteristics as well as better recognition of precursors to problems. Based on control chart

records, observations and correlations with other factors associated with a measurement, breakdown and repair logs, and the information contained in any non-conformance report, procedures can be modified to improve data recovery and usability. In time, the net effect of changes incorporated in standard operating procedures will lead to improvements in performance tests. Along with the identification of limiting factors and the development of solutions, it may be possible to justify raising the analytical level of the measurement based on the quality control indicators.

15A.17 Management Assessment

In addition to the quality control elements in place when a field technique is demonstrated initially, systems need to be in place to insure that data quality is maintained in subsequent measurements once the technique is used routinely. Deployment of a field methodology on a broader scope generally entails use by non-experts, i.e., individuals not associated with the development or implementation of an instrument. For this reason, internal assessments may be needed in the form of independent oversight (audits). The data verification and validation process can be used to insure the fulfillment of QC checks. Ultimately, data may have to be reviewed and approved by individuals who have expertise with the measurement system.

15A.18 Combined Laboratory and Field Measurements

Laboratory and field measurement techniques are not mutually exclusive. They can frequently be used in concert to achieve better and more cost-effective radiological surveys. A likely combination would be reliance on field methods which are faster with the laboratory method serving as a QC check. Appropriate ratios in the number of field to lab measurements would have to be established based on expert judgement and by reviewing the data quality objectives. The ratio could vary from area to area within a site depending upon the situation and the presence of complicating factors.

15A.19 References

International Commission on Radiation Units and Measurements (ICRU), 1994. *Gamma-Ray Spectrometry in the Environment*, Report 53, Bethesda, MD.

16 INSTRUMENT CALIBRATION AND TEST SOURCE PREPARATION

16.1 Introduction

This chapter provides guidance on the important functions of radiation detection instrument calibration and test source preparation. In this chapter, the term "test source" will be used to describe the radioactive material prepared to be introduced into a measurement instrument, and "laboratory sample" will be used to identify the material collected for analysis. Thus, a test source is prepared from laboratory sample material for the purpose of determining its radioactive constituents. "Calibration source" is used to indicate that the prepared source is for the purpose of calibrating instruments.

The continuing validity of calibrations should be checked on a periodic basis (Chapter 18, *Laboratory Quality Control*) as specified in a laboratory's quality assurance manual. This is usually done by counting a check source or some secondary standard in an instrument and comparing the results to those previously obtained when the instrument was known to be in calibration. The frequency and other aspects of calibrations and verifications may be specified in project planning documents (Chapter 4, *Project Plan Documents*) and in analytical statements of work (Chapter 5, *Obtaining Laboratory Services*).

Test sources may be prepared by destructive or nondestructive techniques. A destructive analysis is performed when the original laboratory sample material is altered by ashing or dissolution, which often is followed by chemical separations. Chemical separation usually is necessary when analyzing for specific alpha- or beta-particle emitters. Nondestructive analyses can be used when the laboratory sample is to be analyzed by gamma spectrometry or for gross analyses where the laboratory sample is only dried and counted directly.

The requirements placed upon test source preparation are dictated primarily by the type and energy of the radioactivity to be measured (alpha, beta, or gamma), the radiation detector employed, and—to some degree—whether the measurement is simply a gross radioactivity measurement or if specific radionuclide identification is required. The nature of the laboratory sample material also will have an effect on the test source preparation. These are referred to as "matrix effects" and can be caused by both the chemical and physical characteristics of the laboratory sample. When matrix effects are encountered, one is faced with the choice of altering the analysis methodology for that laboratory sample or possibly flagging the result to indicate a high degree of uncertainty.

The significant characteristics affecting the bias and precision of radioactivity measurements will be discussed in relation to each type of radioactivity. This includes counting efficiency, which can be affected by the characteristics of the test source as well as those of the radiation detector and the geometry of the source relative to the detector. Also, methods used to prepare radioactive test sources for measurement from chemically separated (isolated) radionuclides will be described.

A number of methods and techniques employed to separate and purify radionuclides contained in laboratory samples, particularly in environmental samples, are described in Chapter 14 (*Separation Techniques*), and sample dissolution is discussed in Chapter 13 (*Sample Dissolution*). Instruments that will be used to analyze the test sources prepared as outlined in this chapter are described in Chapter 15 (*Nuclear Counting Instrumentation*). In the case of gross (non-nuclide specific) and nondestructive measurements, chemical separation and purification procedures often are not required. However, to accomplish these measurements, the test source still must be prepared (mounted) in such a manner that the associated radioactivity can be quantified in a reproducible and unbiased manner.

16.2 Instrument Calibration

Instrument calibrations generally are performed for the purpose of establishing the counting efficiency of an instrument. The counting efficiency establishes the number of disintegrations registered in the detector and electronics of a counting instrument compared to the number emitted by the source. Counting efficiencies are specific to the radionuclide (or energy), the geometrical relationship between the source and detector, and a number of characteristics of the source material, especially those that affect absorption and scattering of the radiation. It is common practice to have several different calibrations on a given detector in order to accommodate a number of radionuclides, source-to-detector distances, and counting containers that a laboratory will be required to employ in order to meet project requirements for detection sensitivity, specificity, and the variety of media encountered.

In cases where the efficiency of the detector varies with energy, it is necessary to perform the calibration at a number of energies and establish an efficiency curve that covers the range of energies to be encountered. Some radiation detection instruments require other types of calibrations. These will be discussed under specific instrument calibrations. Generic issues which govern the conduct of calibrations will be discussed below and instrument and test source specific considerations will be provided in the appropriate sections in this chapter.

16.2.1 Standards

Instrument calibration should be performed as needed with only National Institute of Science and Technology (NIST) traceable standards (ANSI N42.23). Calibrations of instruments shall be made using certified reference materials of known and documented value and stated uncertainty. These certified reference materials shall be supplied by:

- NIST directly;
- A standard source supplier whose measurement capabilities or manufacturing processes are periodically tested by NIST; or
- A standard source supplier who documents derived materials with stated uncertainty, and whose value has been verified with analytical and measurement systems that have been tested periodically through an unbroken chain of comparisons to the national standards.

16.2.2 Correspondence

To assure that the instrument calibration is unbiased, calibration sources must be prepared and counted in a manner that assures that they are virtually identical to the test sources in all respects that could affect the counting efficiency determination (ANSI N42.23). The geometry, including the size and shape of the calibration source and counting container (beaker, planchet, vial, etc.) and source-to-detector distance and alignment, must be controlled. Backscatter, scattering, and self-absorption present during test source counting must be duplicated in the calibration process. The density of the calibration source material should be consistent with that of the test sources.

When possible, counting efficiency calibrations should be performed using the radionuclide, whose activity is to be determined in test sources. This may not be possible when the radionuclide is not available as a standard reference material or when gross analyses are performed. When the actual radionuclide is not available, a surrogate radionuclide may be selected that has the same type of particle or photon emission (α, β, or γ) and a proximate energy. When calibrating an instrument in this manner, corrections must be made for any differences between the decay schemes of the two nuclides.

If any factor can vary throughout the test sources, calibrations must be performed which simulate this variability over the range expected to be encountered during test source counting. An example is the necessity to develop a self-absorption curve for alpha or beta counting to account for the changing overall counting efficiency due to absorption in the variable source thickness.

16.2.3 Homogeneity

The calibration source must be prepared in a manner that assures that the material is uniformly distributed throughout its volume. Any deviation from this requirement can result in a calibration that is biased and contributes to the overall uncertainty of the laboratory results.

Liquid calibration sources are more likely to be homogeneous than are solids, particularly those where reference material has been added to a solid material—soil, for example. In order to minimize the overall uncertainty associated with calibration, care should be taken to assure the reference material is thoroughly mixed into the calibration source and distributed uniformly throughout its volume.

16.2.4 Uncertainty

The total uncertainty of calibration is affected directly by the uncertainty associated with the activity of the reference material used in the calibration source. Furthermore, the uncertainties related to the reproducibility of the counting geometry and the non-homogeneity of the calibration source must be considered. Since the uncertainty associated with these factors is difficult to quantify, it should be minimized.

The uncertainty associated with calibration can be reduced by the accumulation of as many counts as practical during the calibration process. The two controllable factors for achieving this are the amount of activity in the calibration source and the counting time allocated for the calibration. As a general rule, at least 10,000 counts should be accumulated during the counting of the calibration source. This may not always be practical when the activity of the calibration source must be limited for reasons listed below.

The activity of calibration sources should be limited to an amount that will not lead to significant dead-time losses and random summing in the instrument being calibrated. Unaccounted for, dead-time losses and random summing could lead to an efficiency determination that is biased and artificially low. In addition, one must be aware of the potential for detector contamination, this is particularly true for semiconductor detectors used for alpha spectrometry.

16.3 General Test Source Characteristics

The goal of test source preparation is to achieve maximum detection capability while introducing minimum bias and uncertainty into the measurement. To realize this goal, test sources must be

prepared in a consistent manner relative to the geometry, disposition of test source material, and the source container.

16.3.1 Geometrical Arrangement

The geometry of a test source must be suitable for the counting instrument and—particularly—it must be reproducible. The radioactivity associated with test sources is measured in geometries that have been standardized by measuring the instrument response to a known quantity of radioactivity in the identical geometry as the calibration source, to the extent possible. Thus, for this standardization to be accurate over time, the test source geometry must remain constant from source to source and with respect to that of the calibration source. This requirement is necessary for performing quantitative and unbiased measurements of all types of radioactivity and for all types of measurement instruments.

16.3.2 Uniformity of Test Source Material

Test source uniformity is related to the physical nature of the source material. Uniformity of test source material relative to its thickness, density (which can be influenced by water content), and homogeneity is important. Nonuniformity can result from a variation in the thickness of the test source material over its cross sectional area. If test sources are deposited in a nonuniform manner, absorption characteristics will vary from source to source and acceptable reproducibility may not be achieved.

Variation in test source thickness or density can have a particularly large effect in the measurement of alpha-particle activity and, because of their smaller mass and charge, a lesser effect in the measurement of beta-particle activity. Alpha and beta test sources, once prepared, often are stored in a desiccator to maintain a constant moisture content. Test source uniformity is relevant to gamma-ray measurements, not because of the absorption of gamma-rays, but because nonuniformity (non-homogeneity) in the distribution of activity throughout a large source changes the effective detection efficiency. For example, if the gamma-ray emitting radionuclides are concentrated in the portion of the test source container nearest the detector, the counting efficiency will be greater than if the radionuclides were uniformly distributed throughout the test source. Thus, test source uniformity can have a large influence on the counting efficiency by which the activity is detected and measured. Measurements of nonuniform sources are not reproducible; thus, radioactive sources of all types must be homogeneous.

16.3.3 Self-Absorption and Scattering

Absorption and scattering within the source material are less important when measuring gamma rays than when analyzing for charged particles. Particulate activity emitted in a source can be scattered by elastic and inelastic collisions with nuclei of the source material, degrading the energy of the particle (self-scatter) or—if sufficiently thick—the particle may be absorbed totally by the source (self-absorption). A scattering/self-absorption factor can be used, however, to correct the measured activity to that of an infinitely thin source. For beta counting, this factor is proportional to $(1 - e^{-\mu x})/\mu x$, where μ is the linear absorption coefficient for beta particles in the test source material and x is the source thickness (Friedlander and Kennedy, 1955, p. 278).

Because of the much smaller mass of beta particles, scattering is more pronounced in sources emitting beta particles than in those emitting alpha particles. Depending on counter geometry, measured beta activity can first increase as the source thickness increases, because of the scattering of electrons out of the source plane and into the detector (Friedlander and Kennedy, 1955, pp. 276-278). At greater thicknesses, self-absorption begins to predominate, and the activity eventually approaches a constant value. When this occurs, the source is said to be "infinitely thick." Counting a source at infinite thickness refers to a measurement made with a source thickness such that further increasing the amount of material added would have no effect on the count rate. The minimum source thickness required for this type of measurement clearly is not more than the maximum range R of the particle in the source material, and is often estimated to be 0.75R (Friedlander and Kennedy, 1955, p. 278).

To assure that scattering does not lead to bias in test source results, it is important that standard sources prepared for determination of counting efficiency and self-absorption corrections are prepared identically in all aspects that affect absorption to test sources whose activities are to be assayed.

Self-absorption increases with the density of the source material and with the size and charge of the emitted particle. Thus, source thickness is of greater concern for measuring alpha particles than for beta-particle emissions and has even less importance in measuring gamma rays, except for low energy x- or gamma rays. Thus, test sources prepared for alpha-particle measurements must be very thin and uniform for maximum detection capability and reproducibility.

The moisture content of the source material will affect the density of the source and the absorption characteristics of the source. A change in source moisture content will alter the density and affect the reproducibility of the measurement. Thus, the amount of moisture within

the test source should be controlled. The following procedures often are followed in order to maintain a low and constant moisture content of test sources to be counted.

- Test sources prepared by coprecipitation are dried by washing the precipitate first with ethyl alcohol and then with acetone while in the filtering apparatus. Suction to the filter apparatus is continued until the test source is dry. The filter with test source is removed from the filtering apparatus, mounted on a planchet, and stored in a desiccator prior to counting.

- Electroplated test sources are dried by heating on a hot plate, in an oven, or under a heat lamp, and then stored in a desiccator until cool and ready to count.

- Laboratory samples analyzed nondestructively are usually dried prior to measurement in order to control moisture content and help ensure that test source characteristics are reproducible. Laboratory samples, such as soil, biota, vegetation, etc., are usually dried in an oven. Test sources not counted immediately, including those for gross alpha and beta measurements, as well as for gamma-ray spectroscopy, should be desiccated to maintain a constant moisture content.

- Evaporated test sources also are stored in a desiccator, after flaming, to maintain a constant moisture content.

Another concern in measuring both alpha and beta particles from deposited test sources is back-scattering: the scattering of particles from the source-mount back through the test source material and into the sensitive part of the detector. Back-scattered beta particles have degraded energies, but can have the apparent effect of increasing the counting efficiency. This may seem to have the desired effect of improving the overall counting efficiency; however, the percent of back-scattered beta particles from the test source must remain constant and be identical to that of the standard source. The magnitude of backscatter is dependent on the beta-particle energy and the thickness, density, and atomic number of the backing material (Faires and Boswell, 1981, p. 220-222). Thus, to reduce the effecf of backscatter on beta-particle measurements, the test source often is mounted on a thin, low Z (atomic number), low density material, as for example aluminum foil or thin organic films (Blanchard et al., 1960). For very precise measurements, a conducting metal film is vaporized onto the organic film so that any electrical charge build up due to the emission of charged particles can be eliminated.

As with absorption, backscatter increases with the thickness of the scattering material up to a saturation level, beyond which it remains constant. The saturation level is reached at a thickness that is about one-third the maximum range of the scattered particle (Faires and Boswell, 1981, p.

221). Therefore, due to the dependency of backscatter on atomic number and thickness, the backing used for the standard source must be identical to that used for the test source mount. For example, if the presence of HCl in the test source requires changing from an aluminum planchet to platinum, a platinum backing must also be used in counting the standard source.

16.3.4 Counting Planchets

A wide variety of planchets made of platinum, nickel, aluminum, and stainless steel can be obtained in various sizes. It is normally not of great importance which type is used as long as several factors are considered (PHS, 1967, p. 20). Some factors that should be considered in selecting a planchet are:

- *Chemical reactivity*. The metal planchet must be inert to the chemicals in the test source, as corrosion of the planchet surface radically alters test source absorption and geometry characteristics.

- *Radioactivity*. The metal comprising the planchet should contain minimal radioactivity and, although this is generally not a serious problem, the planchet background shall be measured.

- *Size*. Two-inch planchets (assuming the detector is at least that large) are often preferred for gross alpha/beta counting to expedite and simplify the evaporation of liquid samples and provide a greater surface area for solid samples, while 1-inch planchets are generally used for alpha spectrometry test samples.

- *Cost*. Platinum planchets should not be used if stainless-steel ones are adequate for the purpose.

It is usually impractical to reuse planchets, and it is generally not recommended. Except for those made of platinum, planchets are inexpensive, and it is not cost effective to clean the planchets and insure they are not contaminated from the prior test source. Platinum planchets are quite expensive and usually can be cleaned effectively in acid and recounted prior to reuse to insure that they are not contaminated.

16.4 Test Source Preparation and Calibration for Alpha Measurements

Several types of instruments are used for counting alpha particles (Chapter 15, *Nuclear Counting Instrumentation*). Each type of instrument has characteristics that affect preparation and mounting of sources. Similarly, these characteristics also affect the calibration of the instrument.

This section discusses the attributes of commonly used instruments and their effects on test source and standard source preparation.

16.4.1 Proportional Counters

Proportional counters (Section 15.2.2.1) often are used to measure alpha particles, particularly when gross analyses are desired. Proportional counters may be "internal," where the test source is placed into the detector or "windowed," where a thin window covers a part of the detector and separates the source from the detector.

16.4.1.1 Alpha Test Source Preparation

Test sources for proportional counters are usually prepared by electrodeposition, coprecipitation, or evaporation, as described below in Section 16.7.6. For internal counters, since the source is placed within the detector, care must be exercised in test source preparation to avoid the inclusion of chemicals which may react with the detector materials. Likewise, any spillage of test source material can result in contamination of the detector.

The absorption of alpha particles in the source material (self-absorption) is quite important when using proportional counters, or other ionization counters, and must be addressed when preparing a test source for counting. Self-absorption is primarily a function of source thickness (t_s) and the range (R_s) of the alpha particles in the source material. For a uniformly thick source, the fraction of alpha particles absorbed by the source increases proportionately to $t_s/2R_s$, when $t_s < R_s$ (NCRP, 1978, pp.104-105). Thus, to approach absolute counting in either 2π or 4π counting geometries, test sources should be prepared as thinly and uniformly as possible.

Another method sometimes used for alpha-emitting test sources in ionization counters is to perform the count at infinite thickness (Section 16.3.3). The count rate of a test source at infinite thickness usually is related to the count rate of a standard source prepared and measured in the exactly the same manner.

Backscatter from alpha sources increases with the atomic number of the backing or source material and with decreasing alpha energy (NAS/NRC, 1962, p. 115). Scattering of alpha particles from the source material itself is not a significant problem, and scattering from the source backing has only a small affect for very thin sources (NCRP, 1978, p. 107). When stainless-steel planchets are used, the increase in a count rate because of alpha backscatter is only about 2 percent (PHS, 1967, p. 19).

16.4.1.2 Proportional Counter Calibration — Alpha

Calibration sources prepared for calibrating counters for a specific nuclide measurement shall contain a radionuclide of similar alpha energy and be measured under identical conditions as the test sources to be measured (ASTM D3648). A variety of radionuclides have been recommended for calibrating for gross alpha analyses (Table 16.1).

TABLE 16.1— Nuclides for alpha calibration

Purpose	Nuclide	Reference
Specific Nuclide and Gross Alpha	^{239}Pu, ^{241}Am, ^{210}Po, ^{228}Th, ^{226}Ra, ^{233}U, ^{235}U, and U_{nat}	ASTM D3648
Gross Alpha	^{241}Am	EPA ,1980
Gross Alpha	^{241}Am, ^{237}Np, and U_{nat}	ASTM D1943
Gross Alpha	^{241}Am, ^{239}Pu, ^{230}Th, and U_{nat}	APHA (1995), Method 7110

To the extent possible, standard sources should be prepared in a manner identical to the method used for test source mounting. The counting efficiency (ε) is then determined by counting the standard source for a sufficient time to accumulate approximately 10,000 counts and dividing the derived counts per second (cps) by the α emission rate of source in disintegrations per second (dps).

$$\varepsilon = \frac{cps}{dps}$$

In cases where finite test source thicknesses are unavoidable, alpha-source counts can be adjusted to account for self-absorption (PHS, 1967, p. 19). This requires that a self-absorption curve be prepared in order to determine the change in counting efficiency as a function of source thickness or mass. Standard sources containing a known amount of the radionuclide of interest are prepared in varying thicknesses (mass) and counted. Absorption curves for gross alpha-particle measurements most often are constructed using reference material containing one of the nuclides listed above. The absorption curve is constructed by counting planchets containing varying mass of material but with constant added radioactivity. A curve is generated by plotting the efficiency at a given source thickness divided by the efficiency at "zero" thickness versus source mass (mg) or density thickness in $\mu g/cm^2$ or mg/cm^2 (NCRP, 1978, p. 105). Thus, the efficiency relative to the "zero thickness" efficiency can be read directly from this curve for any measured test source thickness. Test sources prepared for gross measurement are counted in the exact geometry as those used to prepare the absorption curve. The material forming the matrix for the self-absorption standard source should, when possible, be identical to that expected in the test sources to be analyzed. Based on the test source mass or density thickness in units of $\mu g/cm^2$ or mg/cm^2,

the correction factor determined from the absorption curve is applied to the test source count, yielding the count rate equivalent to an infinitely thin source.

Most modern proportional counters are capable of simultaneous alpha and beta counting. This is accomplished by identifying the two types of particles based on their pulse height. Those pulses whose heights exceed an experimentally established discriminator level are registered as alpha counts and those falling below this level are recorded as beta counts. Some fraction (usually less than 10 percent for a weightless source) of the alpha particles is recorded as betas, even for nearly weightless test sources. This fraction increases as the thickness (mass) of the source increases. A much smaller (often insignificant) fraction of the beta interactions are registered as alphas. This misclassification of alpha and beta counts is referred to as "crosstalk."

For simultaneous alpha and beta counting, corrections must be made to the beta count rate to remove the portion contributed by alpha particles. Since the fraction of alpha counts occurring in the beta channel is a function of the source mass, a crosstalk curve relating the fraction of alpha particles counted as beta to source mass must be developed. This can be accomplished concurrently with the self-absorption calibration if the radionuclide selected is an alpha emitter only—no beta particles. This is done by recording the beta counts from the alpha self-absorption determination at all source weights and plotting the fraction (beta counts/alpha + beta counts) as a function of source mass (Section 17.4.1). Beta count rates then can be corrected for the influence of the alpha particles at all source thicknesses.

16.4.2 ZnS(Ag) Scintillation Counter

This type of counter is discussed in Section 15.2.2.3. Because the alpha particle must be emitted from the source and interact with the screen, as it does with the ionization chamber of an internal proportional counter, the previous description concerning self-absorption and scatter of alpha particles during analysis in an internal proportional counter may be applied to counting alpha particles with a ZnS(Ag) scintillation counter. Additional advantages of this counting arrangement are the very low backgrounds that are achievable and the small potential for permanently contaminating the counter, because the zinc sulfide screens can be replaced.

A source mount shaped like a washer, with one side enclosed with a transparent ZnS(Ag) screen, is an arrangement often used. The test source to be counted is placed in the hole of the "washer," in contact with the ZnS(Ag) screen. The other side of the test source mount is sealed, generally with wide transparent tape, securing the test source within the source mount. The test source is then placed on an appropriately sized photomultiplier tube and counted. Because of the

availability of large photomultiplier tubes, sources up to 5 inches in diameter can be prepared for measurement (PHS, 1967, p. 26).

The considerations related to alpha calibrations, discussed above under proportional counters, apply equally to scintillation counter calibration.

16.4.3 Alpha Spectrometry With Semiconductor Detectors

Semiconductor detectors for alpha particle counting are discussed in Section 15.2.2.5. Alpha-energy spectra of very high resolution are attainable with semiconductor detectors if the prepared test source is essentially weightless, ≤ 1 $\mu g/mm^2$ (Herpers, 1986, pp. 143-145). As the thickness of the test source increases, the spectral energy is degraded due to self-absorption, which broadens the peak and forms a "tail" on the lower-energy side (Chapter 17). The alpha-energy spectral degradation will increase, as the source thickness increases, raising the possibility of overlapping peaks with a loss of spectrum integrity. Thus, it is of utmost importance to prepare very thin and uniform alpha test sources for spectrometry. This may be accomplished by electrodeposition or coprecipitation (ASTM, D3084), if reagents are controlled so that only small (milligram) quantities of precipitate are recovered (Sections 16.6.1 and 16.7.2). For example, in the coprecipitation of actinide test sources for spectral analysis, source thicknesses of 0.4 to 1 $\mu g/mm^2$ (0.04-0.1 mg/cm^2) are routinely achieved, which is quite adequate for producing well-defined alpha spectral peaks (EPA, 1984a).

Semiconductor detectors used for alpha spectrometry require both efficiency and energy calibrations. Calibration sources, traceable to NIST, often are prepared with multiple radionuclides so they may be used for both types of calibration (ASTM D3084). Sources containing ^{234}U, ^{238}U, ^{239}Pu, and ^{241}Am have been used for this purpose. When mixed-nuclide calibration sources are used, the average counting efficiency is often calculated using the efficiencies of the individual radionuclides. Some alpha spectrometry analysis programs calculate an average efficiency where the individual radionuclide efficiency is weighted by the uncertainty in its determination. Other radionuclide combinations may be used, but in addition to the requirement for traceability for the disintegration value, the energies of the radionuclides must be known with a high degree of certainty.

Calibration sources may be prepared by either electrodeposition or coprecipitation. Due to their durability and stability, electrodeposited calibration sources are often chosen. It is important that the area of deposition be consistent with that of test sources to be counted and that there are no significant impurities present (ASTM D3084). See the additional discussion on alpha spectrometer calibration in Section 17.3.2.

16.4.4 Liquid-Scintillation Spectrometer

With proper scintillators, liquid scintillation can be used to measure alpha-particle emitters (Passo and Cook, 1994) (Section 15.2.2.4). Although the relatively high background of liquid scintillation counting restricts the sensitivity relative to other counting techniques, e.g., internal proportional counting or the use of ZnS(Ag) screens, the ease of source preparation and the nearly 100 percent counting efficiency are advantages often exploited (Hemingway, 1975, p. 146). The separation of alpha- and beta-particle counts attained in the spectrometer can be enhanced by proper scintillator choice. Ultima Gold AB™ was designed specifically to maximize alpha/beta separation in aqueous solutions and, in other studies, poor alpha/beta separation has been overcome by making the standard cocktail 20 percent in naphthalene (Passo and Cook, 1994, pp. 3-11 to 3-12). It is believed that naphthalene improves the alpha/beta separation by acting as an intermediate in the energy transfer process between the solvent and the fluor (McDowell, 1986).

EPA's (1978) recommended procedure for measuring ^{222}Rn in water uses liquid scintillation counting. The protocol is based on the solubility of radon in a number of scintillators. To measure radon in air, the radon is first adsorbed onto activated charcoal and then mixed with an appropriate scintillator and counted (EPA, 1987; Passo and Cook, 1994, pp. 8-5 to 8-10). Utilizing the high solubility of ^{222}Rn in organic solvents, concentrations of ^{222}Rn in air have been determined by bubbling air through the scintillator in a scintillation vial (Amano et al., 1985). Concentration of ^{222}Rn, determined by liquid scintillation, also can be used in the measurement of its parent, ^{226}Ra.

Some actinides (U and Th) and transuranics (Np, Pu, Am, and Cm) have been measured by a procedure that involves "Extraction Scintillation Techniques" (Passo and Cook, 1994, pp. 6-1 to 6-2 and 13-1 to 13-6). An extraction agent, e.g., bis(2-ethylhexyl) phosphoric acid (HDEHP), is mixed either with a toluene or a di-isopropylnaphthalene (DIN) based cocktail. The alpha emitter, in the aqueous laboratory sample, is extracted into the scintillation mixture and counted by liquid scintillation. The discussion in Section 16.5.2.1 can be applied to both alpha and beta particles.

16.5 Characteristics of Sources for Beta Measurements

16.5.1 Proportional Counters

Beta decay generally is accompanied by gamma-ray emission; the latter normally is much easier to identify and quantify. Beta-particle counting typically is more difficult, due to the additional

source preparation and associated complications resulting from the effects of backscatter, scattering, and absorption in the source material (NAS/NRC, 1962, p. 118-119). Beta particles are not emitted monoenergetically and may result in additional difficulty in quantitative measurements.

Beta counting in ionization-type counters often is used after chemical separations are performed to isolate the beta-emitting radionuclide of interest from other radionuclides. Beta measurements are performed on chemically isolated pure beta emitters (beta decay not accompanied by a gamma-ray) and also in cases when increased sensitivities are required to meet detection limits, such as, ^{89}Sr, ^{90}Sr, ^{99}Tc, ^{131}I, ^{134}Cs, and ^{137}Cs (EPA, 1980). The proportional counter often is used for measuring these beta-particle emitters. Test sources measured in a proportional counter are usually prepared by electrodeposition, coprecipitation, or evaporation, as described below in Section 16.7 (Blanchard et al., 1960). The comments on chemical reactivity of source contained materials and contamination given in Section 16.3.1, apply here.

16.5.1.1 Beta Test Source Preparation

Although it remains a consideration, self-absorption of beta particles is not as pronounced as with alpha particles, because the charge and mass of beta particles are significantly smaller. Scattering, and particularly backscatter from the source mount, is much more pronounced for beta counting than for alpha counting (Blanchard et al., 1957). To reduce scatter, plastic mountings are often used to mount sources for beta counting (EPA, 1980). The effects resulting from self-absorption and scattering can be minimized by preparing test sources in a standardized constant thickness, or using a correction factor based on an empirical calibration curve for different thicknesses (Friedlander and Kennedy, 1955, pp. 276-277; Tsoulfanidis, 1983, pp.133-134). (Section 16.3.3.)

For sufficiently thick sources, the beta particles emitted from the source reach a limit, and the count rate becomes independent of the source thickness.

16.5.1.2 Proportional Counter Calibration — Beta

As in other calibrations, proportional counters used for beta-particle analysis shall be calibrated with NIST traceable standards in a manner that is totally consistent with the counting of test sources. When possible, the radionuclide to be quantified should be used as the calibration source. For gross beta analysis, the radionuclides presented in Table 16.2 have been recommended for calibration sources.

TABLE 16.2 — Nuclides for beta calibration

Purpose	Nuclide	Reference
Gross Beta	^{137}Cs	ASTM D3648
Gross Beta	^{137}Cs	EPA, 1980
Gross Beta	^{137}Cs	ASTM D1890
Gross Beta	^{137}Cs and ^{90}Sr-^{90}Y	APHA (1995), Method 7110

If test sources of varying mass are to be counted for beta activity determination, a self-absorption curve must be prepared. The method used is identical to that described under alpha calibration for proportional counters, except that a beta-emitting reference material is used instead of alpha.

16.5.2 Liquid-Scintillation Spectrometers

When beta measurements are required, especially those involving pure beta emitters of low energy, they are often performed in a liquid scintillation spectrometer, because self-absorption and backscatter are eliminated and counting efficiencies are relatively high (Herpers, 1986, pp. 133-135). Although it is the preferred instrument to measure low-energy, pure beta-emitting radionuclides, e.g., ^{3}H, ^{14}C, and ^{35}S, it is a well-established procedure for measuring numerous other beta-emitting radionuclides, including ^{45}Ca, ^{65}Zn, ^{141}Ce, ^{60}Co, ^{84}Sr, ^{55}Fe, ^{87}Rb, ^{147}Pm, and ^{36}Cl (Hemingway, 1975, pp. 145-146). The liquid scintillation spectrometer, applied to beta-particle measurements, is described in detail in Section 15.3.3.

Tritium is the radionuclide most often measured by liquid scintillation counting (DOE, 1997; EPA 1979; Lieberman and Moghissi, 1970, p. 319). The primary step in preparing water samples for counting is distillation in the presence of an oxidizing agent, such as $KMnO_4$, to separate the tritium labeled water from dissolved solids, including interfering radionuclides, and any organic material that may be present. An aliquant of the distillate is then mixed with a liquid scintillator and counted in a liquid scintillation spectrometer. To measure tritium in samples of other matrices, the water in the sample can be removed and collected by distillation as an azeotrope with, for example, *n*-hexane or cyclohexane (Moghissi, 1981; EPA, 1979). An aliquant of the water collected is then mixed with a liquid scintillator and counted, as described above for water samples.

Tritium can be concentrated in a sample of water if lower detection limits are required. The concentration process, electrolysis, uses the isotopic effect caused by the large mass difference (three times) between ^{1}H and ^{3}H (DOE, 1997; EPA, 1984a). Tritium becomes enriched as electrolysis continues. Generally, 50 mL of the laboratory sample is placed in an electrolysis cell and a current of about three amps applied. Electrolysis is continued until the volume reaches

about 5 mL. More sample can be added to the cell during the electrolysis, if greater sensitivity is necessary for the measurement. The concentrated laboratory sample is then distilled in the presence of an oxidizing agent, such as $KMnO_4$, and treated like a water sample (see above).

16.5.2.1 Liquid Scintillation Test Source Preparation

The preparation of a laboratory sample for a liquid-scintillation spectrometer usually is relatively simple and fast. The radionuclide to be measured is isolated in a solution, which is then introduced into and thoroughly mixed with one of a variety of ready-to-use commercially available liquid scintillators. This mixture is often referred to as a scintillation "cocktail." The liquid scintillator is an emulsion system, usually consisting of an aromatic solvent containing the appropriate scintillator mixed with a detergent (NCRP, 1978, pp.168-169). If a sample is insoluble in the scintillator, it can be ground to a fine powder, stirred into the scintillator until a homogeneous mixture is formed, and solidified with a gelling agent (Friedlander et al., 1981, p. 303).

Because much or our ecosystem consists of materials composed of carbon and hydrogen, the measurement of ^{3}H and ^{14}C levels in biological materials is important. Water, for ^{3}H analysis, can be recovered efficiently from all types of environmental and biological samples by azeotropic distillation. The laboratory sample is distilled with a hydrocarbon, such as benzene or cyclohexane, which is compatible with the liquid scintillation process (Moghissi et al., 1973; Moghissi, 1981). The distillate is mixed with the proper scintillator and counted in a liquid scintillation counter. Tritium has been successfully measured by this technique in such samples as animal and human tissues, soil, hay, grass, urine, and milk.

Environmental and biological samples also can be analyzed for total ^{3}H (that contained in both the water and fibrous fractions) by quantitatively combusting the laboratory sample, collecting the water formed, and analyzing it by liquid scintillation spectrometry (DOE, 1997). In another case, both ^{3}H and ^{14}C can be measured simultaneously (EPA, 1984b). The laboratory sample first is freeze-dried to remove and collect the water fraction. The tritium in the water is measured directly by liquid scintillation spectrometry. The fibrous (freeze-dried) material is combusted and the H_2O and CO_2 are collected. As before, the ^{3}H in the water is measured directly by liquid scintillation spectrometry, while the ^{14}C is first converted to benzene or captured as CO_2 and then counted by liquid scintillation spectrometry.

A primary problem with measurements using a liquid-scintillation spectrometer is "quenching." Quenching occurs when the production of light is inhibited or the light signal is partially absorbed during the light transfer process by a substance in the liquid. The two basic types are

chemical and color quenching. Some of the stronger chemical quenchers are alkyl bromides, iodides, nitrates, mercaptains, and ketones (NCRP, 1978, p. 46). Color quenching involves the reduction of light transmission through the solution to the cathode of the phototube by the absorption of the light photons. The two techniques most often used to correct for quenching involve the use of internal or external standards.

Chemiluminescence, the production of light by a chemical reaction, can be troublesome in liquid-scintillation counting. However, the duration of chemiluminescence is generally short, and a wait of a few minutes after mixing the reagents will allow the effect to dissipate before counting starts. Similarly, phosphorescence, the emission of light from certain chemicals caused by exposure to light, will cease a short time after being placed in the dark. This is referred to as "dark adapted" (Faires and Boswell, 1981, p. 182).

16.5.2.1 Liquid-Scintillation Spectrometer Calibration

When the quenching of a group of test sources is predictable, e.g., distilled drinking water (EPA, 1980; ASTM D4107), a counting efficiency is determined for the group by placing a known quantity of reference material in the source medium and scintillation solution under identical conditions (vials and volumes) as the sample medium.

Except for test sources with very predictable amounts of quenching, it may be necessary to determine a counting efficiency for each laboratory sample. Two methods of determining counting efficiency are available: internal standardization and external standardization (NCRP, 1978).

Internal standardization for quench correction is by the method of standard additions. This involves the counting of two aliquants of a sample, one being the sample and the other is an identical aliquant that has been spiked with a known amount of the radionuclide being determined. The degree of quench can then be determined from the spiked aliquant and applied to the unspiked sample (DOE, 1995). This method does not require a curve for correction but decreases throughput because two test source counts are required. For these reasons, the use of an external standard is the more widely used technique to correct for quenching (Horrocks, 1973).

One external standard method is also called the "external-standard channels-ratio" (Baillie, 1960; Higashimura et al., 1962). In this method, a series of vials is prepared containing a known amount of reference material and varying amounts of the medium being evaluated. Windows in the energy spectrum are set for a high- and low-energy region. The vials are counted and the ratios of low-to-high count rates are recorded for each quenched source. A quench curve is then

prepared by plotting the ratios of low-to-high energies as a function of counting efficiency. The efficiency of an unknown test source can then be determined from its low-to-high energy ratio during counting.

The second external-standard method employs an external gamma-ray source that generates Compton electrons in the scintillation solution. Count rates from the external source are determined for a set of sources whose efficiency is known from the internal-standard method. A quench curve is then prepared by plotting the external count rate vs. counting efficiency.

The external-standard methods should not be generalized beyond use for the media conditions under which they were prepared.

16.6 Characteristics of Sources for Gamma-Ray Measurements

Backscatter and self-absorption, which must be addressed when measuring alpha and beta emissions, cause less uncertainty in the measurement of most gamma-ray emitters. This is because the penetrating nature of gamma rays is totally different from that of particles. For thick samples or high-Z matrices, a detection-efficiency correction is necessary for low-energy photons (especially below 200 keV) due to the self-absorption of photons in the sample. There is, however, some backscatter of gamma-rays from the shield surrounding the detector, which produces a small peak at about 200 keV (NAS/NRC, 1962, p. 32).

16.6.1 Gamma Test Source Preparation

No significant precautions usually are required in preparing test sources for gamma-ray spectrometry, as long as the test source is homogenous and positioned reproducibly relative to the detector. Although source properties (e.g., density and moisture content) are not as important in gamma-ray spectrometry as in alpha or beta measurements, test source preparation for gamma measurements may still include drying and ashing to control moisture content and to reduce the test source size. Homogeneity of the test source can be attained by thoroughly mixing laboratory samples that have been ashed (many combustible matrices not containing volatile radionuclides are ashed), by grinding and mixing solids (e.g., soils and sediments), or by finely chopping and mixing fresh vegetation. Also, calibrations are generally conducted using standard sources with identical counting geometries and the same or similar matrices as the test source for analysis.

Important considerations in preparing test sources for gamma-ray spectrometry are geometry (shape), size, and homogeneity (uniformity) of the source. Test sources can be in any reproducible shape or size, but the radionuclides must be uniformly distributed throughout. A

counting container that allows the source to surround the detector, thus maximizing the geometrical efficiency, is referred to as the "Marinelli" or "reentrant" beaker (Hill et al., 1950). It consists of a cylindrical sample container with an inverted well in the bottom of the beaker that fits over the detector.

Counting efficiencies are determined by measuring a known quantity of the radionuclide(s) of interest in the same matrix and source-detector configuration as the sources requiring analysis (NCRP, 1978, pp. 243-244; ASTM, D3649). This eliminates any effect that might be caused by differences in test and calibration source characteristics, e.g., density, moisture content, shape, and size. Efficiency curves may be prepared for a detector by measuring a variety of standardized sources having different photopeak energies under identical conditions as the unknown (Coomber, 1975, p. 18; ANSI, 1991).

Two important advantages of gamma-ray spectrometry are the ability to measure more than one radionuclide simultaneously and the elimination or reduction of the necessity for chemical dissolution and radionuclide separations (nondestructive analysis). Source configurations for nondestructive analyses generally are selected to optimize counting efficiency. Examples are (PHS, 1967, p. 78):

- Marinelli beakers of various volumes to measure liquid sources, as water, milk, and food samples blended to a slurry;
- Cylindrical plastic containers of various volumes, such as the 400 mL "cottage-cheese container" frequently used for containing solid sources;
- Planchets of various diameters to measure precipitates, air filters, etc.; and
- Aluminum cans of a standardized volume into which solid sources can be compressed, and sealed, if desired, to retain radon.

If greater counting efficiency is required, the test source size can be reduced, allowing a greater amount of the laboratory sample to be counted and in a more favorable geometry. Examples of such processes are:

- Reducing the volume of water samples by evaporation;
- Reducing the volume of water samples by co-precipitating the desired radionuclides;

- Reducing the size of vegetation samples by compression into a large pellet or by ashing, if volatile radionuclides are not of interest; and

- Reducing the size of filter samples by compressing the sample into a reduced standard volume or by ashing, if volatile radionuclides are not of interest.

16.6.2 Gamma Spectrometer Calibration

Most gamma-ray spectrometry systems are calibrated with either single or mixed standards in an exact matrix and geometric form as the samples to be analyzed. However, there are computer codes that can calculate detector efficiency from the physical dimensions of the detector and sample counting geometry (Mitchell, 1986; Hensley et al., 1997).

Commercial standards of single or mixed gamma-ray emitters in a matrix of known chemical composition and density can be prepared in user-supplied containers. Calibrations based upon these standards can then be adjusted to correct for any differences in composition and density between the calibration source and the test source (Modupe et al., 1993).

MARLAP recommends that calibration data for gamma spectroscopy calibration be obtained from the National Nuclear Data Center at Brookhaven National Laboratory (http://www.nndc.bnl.gov/nndc/nudat/). Calibration data are readily available for common radionuclides, including ^{210}Pb, ^{241}Am, ^{109}Cd, ^{57}Co, ^{141}Ce, ^{139}Ce, ^{203}Hg, ^{51}Cr, ^{113}Sn, ^{85}Sr, ^{137}Cs, ^{54}Mn, ^{88}Y, ^{65}Zn, ^{60}Co, and ^{40}K. For more information on gamma spectrometry calibration see ANSI 42.14. (Also see Section 17.3.1.6 on gamma calibration.)

16.7 Methods of Test Source Preparation

16.7.1 Electrodeposition

High-resolution spectroscopy requires a very thin, uniform, flat, and nearly weightless source mount. Ideally, the source plate to determine alpha activity by a spectrometer would be a flat plate coated with a monolayer of radioactive atoms and with no foreign material above the layer to attenuate the alpha radiation (Kressin, 1977). The electrodeposition of radionuclides on a suitable metallic surface from an aqueous solution often can produce thin and uniform test sources that approach these ideal conditions. Thus, this technique is very appropriate for preparing sources of alpha emitters, especially the actinides, which include uranium, plutonium, thorium, americium, and neptunium (ASTM, D3865; DOE, 1997; EPA, 1979).

There are a number of electrolytic cell designs used to electrodeposit radionuclides. The cathode, on which the radionuclide deposits is often a thin metal foil or disc, such as platinum or stainless steel, or a metal-coated plastic film (Blanchard et al., 1960). The stirring rod, often made of platinum, can also serve as the anode of the cell. Deposition of actinides for alpha spectrometry also has been performed on disposable cells constructed form 20 mL polyethylene scintillation vials and highly polished stainless steel planchets (Talvite, 1972). Disposal prevents cross contamination. The composition of the electrolyte and the parameters applied in the electro-deposition process, such as applied voltage, amperage, current density, and deposition time, are dependent upon the chemical properties of the element, especially its reduction potential, and foreign material that might be present. Thus, "Each element requires optimization of its own procedure" (Adloff and Guillaumont, 1993, p. 158). Deposition time varies from 10 minutes to two hours.

Actinides and similar elements are extremely hydrolytic and can deposit on the glass cell wall or anode or precipitate during deposition (Puphal et al., 1983). Electrodeposition typically is performed, therefore, in electrolytic solutions at low pH (≈2) to prevent hydrolysis or precipitation. The solution may contain complexing agents (such as fluoride) and chelates (such as EDTA) to minimize the effect of interfering ions, commonly encountered in biological and environmental samples (Puphal and Olsen, 1972). The procedure of Kressin (1972), however, illustrates the admonition of Adloff and Guillaumont cited above: citrate and fluoride, a chelate and complexing agent, respectively, each interferes with the electrodeposition of plutonium and americium in his process.

Electrodeposition is applicable to more than 30 radionuclides. The main advantage of electrodeposited sources over those from other methods of preparation is their extremely thin, uniform deposit of a radionuclide on a plate, which permits high resolution spectroscopy; however, the yield is often not quantitative (Adloff and Guillaumont, 1993, p. 158). Thus, the yield must be monitored with the inclusion of a known quantity of an isotope, which is deposited simultaneously with the analyte. Radioactive sources of the following elements have been prepared successfully by electrodeposition (DOE, 1997; Blanchard et al., 1960; Johnston et al., 1991.)

Actinium	Gold	Polonium	Strontium
Americium	Hafnium	Promethium	Tellurium
Antimony	Indium	Protactinium	Thallium
Bismuth	Iron	Radium	Thorium
Cadmium	Lead	Rhenium	Tin
Cobalt	Neptunium	Ruthenium	Uranium
Copper	Nickel	Selenium	Yttrium
Curium	Plutonium	Silver	Zinc

Particularly important to environmental analysis is a procedure by which virtually all alpha-emitting nuclides—radium through californium—can be determined in soil in any combination on a single sample with few interferences using electrodeposition to prepare the source (Sill et al., 1974).

Although sources of radioactive isotopes of these elements have been prepared by electro-deposition, it might not be the preferred technique in some of the examples cited. For various reasons, other methods of test source preparation may be superior: yields can be low, the presence of other metals sometime interferes, the quality of deposition might be poor (flaking), the recovery can be low, the spectral resolution might be poor, and some procedures require rather elaborate equipment, are expensive, and are time consuming, thus labor intensive (Sill and Williams, 1981; Hindman, 1986). Interference will be caused by several factors: (1) "Any element present in the separated fraction that is able to be electrodeposited will be present on the metal disc;" (2) "Incomplete separation of rare earth elements or incomplete wet ashing for the removal of organic material will decrease the efficiency of the electrodeposition and may result in a thick deposit unsuitable for α-spectrometry measurement;" and (3) "Samples containing more than 20 μg of U are unsuitable for measurement by α spectrometry due to the thickness of the deposit" (DOE, 1997, p. 4.5-270). When stainless-steel planchets cannot be used, because of the corrosive nature of the electrolyte, and platinum is required, the method can be quite expensive and time consuming, since recycling of the expensive electrode material requires thorough cleaning to prevent cross contamination.

Test sources of actinides are often prepared by electrodeposition with yields of 90 percent and higher (DOE, 1997; EPA, 1979; Sill et al., 1974; Puphal and Olsen, 1972; Kressin, 1977; Talvite, 1972; Mitchell, 1960; Shinohara and Kohno, 1989, pp. 41-45). In addition, ^{54}Mn sources have been successfully prepared by the electrodeposition from mixed-solvent electrolytes onto stainless steel planchets (Sahoo and Kannan, 1997, pp. 185-190).

If the redox couple between the metal cathode and the radionuclide to be deposited is positive, the radionuclide will deposit spontaneously. That is, it will deposit quantitatively without using any applied potential. Generally, a metal planchet is simply suspended in the solution that is stirred with a glass stirring rod for a few hours (Blanchard, 1966; DOE, 1997). An example of such a spontaneous reaction between polonium and nickel is given below.

$$Po^{+4} + 2\ Ni \rightleftharpoons Po + 2\ Ni^{+2} \qquad E^{\circ} = 0.98\ Volt$$

Polonium also will deposit quantitatively on silver planchets. ^{210}Po is an important naturally occurring radionuclide that is often included in environmental studies. Spontaneous deposition

onto either nickel or silver is the preferred technique for preparing ^{210}Po sources for measurement.

A similar technique, called internal electrolysis, is preformed by selecting electrodes that have a large difference in potential. A conventional electrolytic cell containing an acid solution of the radionuclide to be deposited may be used. A magnesium ($E^\circ = +2.37$ volts) strip, for example, is inserted into the electrolyte and connected by an external circuit to the inert metal cathode (planchet), usually platinum. A spontaneous current flows and deposition on the cathode will occur. The conditions at the inert cathode are exactly the same as if an external voltage were applied; however, longer electrolysis times are necessary to achieve quantitative recoveries. Very thin and uniform sources of ^{106}Ru, ^{110}Ag, ^{203}Hg, ^{60}Co, ^{114}In, ^{51}Cr, ^{198}Au, and ^{59}Fe were prepared by this technique, with greater than 96 percent recovery in all cases (Blanchard et al., 1957, pp. 46-54; Van der Eijk et al., 1973).

16.7.2 Coprecipitation

Coprecipitation (Section 13.8) has been employed to mount sources for alpha spectrometry. Some radiochemists prefer the method to electrodeposition, maintaining that, "The procedure is faster and more reliable than those involving electrodeposition and gives consistently higher yields" (Sill and Williams, 1981). Hindman (1986) asserts that the method is "more rapid, more economical, and more efficient" ... "and yields good decontamination factors, high recoveries, and excellent resolution of the α spectra for uranium, plutonium, americium, and thorium."

Although sources prepared by coprecipitation are thicker than those prepared by electrodeposition, sufficiently thin sources, even for alpha spectrometry, can be prepared by controlling the amount of precipitate formed. Sources thinner than 0.5 $\mu g/mm^2$ can be prepared of the actinides by coprecipitation (EPA, 1984a). Thicker sources lead to poor resolution of the spectra (Hindman, 1983) and sources produced by any technique that are greater than 10 $\mu g/mm^2$ lead to attenuation of alpha particles (Adolff and Guiallaumont, 1993, p. 161).

After separations are completed, a slurried precipitate is poured quantitatively through a filtering apparatus collecting the precipitate on a small (e.g., 25 mm dia.) filter. Vacuum filtration often is used to speed the operation. With suction applied, the precipitate typically is washed with water, then ethyl alcohol, and finally with acetone to dry the precipitate. The filter is removed from the filtering apparatus and mounted on a metal planchet, commonly with double-stick tape, and stored in a desiccator to await counting. Any ^{222}Rn progeny that collects on the filter during the filtration process will decay in a short period of time and not affect the measurement. Samples of the following radionuclides have been prepared for quantitative analysis by coprecipitation:

Radionuclide	Carrier	References
^{32}P	$MgNH_4PO_4$	a
^{51}Cr	$BaCrO_4$	a
$^{89/90}Sr$	$SrC0_3$	a,b,c
^{90}Y	$Y_2(C_2O_4)_3$	a,b,c
^{131}I	PdI_2	a,b,c
^{137}Cs	Cs_2PtCl_6	b
^{147}Pm	$Nd_2(C_2O_4)_3$	a
^{210}Bi	BiOCl	a
^{226}Ra	$BaSO_4$	b
Th	$Ce(IO_4)_4$	d
Th	LaF_3	a,b
U	LaF_3 (NdF_3)	a,b,(f)
Np	LaF_3	b
Pu	LaF_3(NdF_3)	a,b,d,(f)
Am	LaF_3(NdF_3)	a,b,d,(f)
Cm	LaF_3	b
Th	$Ce(OH)_2$	e
Np	$Ce(OH)_2$	e
Pu	$Ce(OH)_2$	e
Am	$Ce(OH)_2$	e
Cm	$Ce(OH)_2$	e
U	UF_3	e

a EPA (1984) c DOE (1997) e Sill (1981)
b EPA (1980) d Hindman (1983) f Hindman (1986)

It should be emphasized that precipitated sources must be thoroughly dry before measurement, otherwise, self-absorption and scattering will change with time as water evaporates. Also, sources are often covered with a thin film, such as Mylar™ or Formvar™, to avoid sample loss and contamination of counting equipment. Care must be taken to avoid excessive handling of the source that can change the physical nature of the co-precipitate, producing an uneven thickness.

Another precipitation technique has been applied to preparing radioactive sources. Source preparation by precipitation can be conducted in a desiccator fitted with a valve to allow first the evacuation of the desiccator and then the admission of a precipitating gas, such as ammonia (NH_3) or hydrogen sulfide (H_2S) (Blanchard et al., 1957, pp. 26-31; Van der Eijk et al., 1973). A carrier is added to the sample and a know quantity is pipetted onto a planchet. The planchet containing the test source solution is placed in the desiccator and exposed to a precipitating gas for one to two hours. This period of time allows settling to occur. The test source is removed from the desiccator and evaporated beneath a heat lamp. Using an $AlCl_3$ carrier in an ammonia atmosphere, Yoshida et al. (1977) prepared uniformly deposited radioactive sources of ^{59}Fe, ^{60}Co, ^{95}Nb, ^{103}Ru, and ^{198}Au by this technique.

16.7.3 Evaporation

When a high degree uniformity of the deposit is not a requirement for the measurement, sources can be prepared by simple evaporation under a heat lamp (Bleuler and Goldsmith, 1952). This procedure is easy, fast, and adequate for many type measurements. Water samples for gross alpha and beta screening measurements are often prepared by this method (EPA, 1984a; EPA, 1980). An aliquant of the water laboratory sample is evaporated on a hot plate until only a few milliliters remain. The concentrated solution that remains is then transferred quantitatively with a pipette to a tared stainless-steel planchet, usually 2-inch diameter, and evaporated to dryness under a heat lamp. The planchet, with the evaporated test source, is then flamed over a burner until dull red to reduce the amount of solids present and to convert the matrix to an oxide. (Insoluble hydroxides, which are often bulky and gelatinous, are prime candidates for ashing, as the oxide formed is much firmer, more uniform, and better defined.) The test source is cooled, weighed, and counted for alpha and beta particles in a proportional counter. Planchets containing evaporated solids cannot be flamed if volatile radionuclides are to be measured.

Most of the solids in an evaporated source deposit in a ring around the edge. Techniques to improve uniformity include the addition of a wetting agent, such as tetraethylene glycol or a 5 percent insulin solution (Shinohara and Kohno, 1989), freeze drying the sample, or precipitation and settling of the active material prior to evaporation (Friedlander et al., 1981, p. 305; Van der Eijk and Zehner, 1977). The wetting agent is pipetted onto the spot to be covered by the test source, then removed with the pipette. That remaining can be dried under a heat lamp. A known quantity of the laboratory sample is then pipetted onto the spot and dried under a heat lamp. Additional portions of the sample may be added and evaporated.

Sample spreading on the planchet, as it is heated, can result in depositing test source material on the planchet walls or in the flow of the liquid over the edge of a flat, lipless planchet. Such spreading can be controlled or restricted by outlining the desired source area with a wax pencil. Metal planchets often are constructed with a small lip around their circumference that retains the test source on the planchet. All sources prepared by evaporation should be flamed to a dull-red color, cooled, and stored in a desiccator until counted, unless they contain volatile radionuclides, in which case simply store the evaporated test source in a desiccator.

Source spreading during evaporation has been restricted by electrospraying a silica gel suspension onto a thin film to produce a circular pad. The radioactive source solution is dropped onto the circle and evaporated to dryness (Chen et al., 1989).

EPA's (1980) prescribed Method 900.0 for measuring gross alpha and beta radioactivity in drinking water suggests that the sample aliquant be limited to what will produce 5 mg/cm^2 of solids on the planchet. Thus, for a 2-inch planchet (20 cm^2), an aliquant containing 100 mg of non-volatile dissolved solids is the recommended maximum test source mass.

After a radionuclide in solution has been purified by chemical techniques, i.e., impurities removed, the solution can be transferred to a planchet and evaporated to dryness, as described above. Evaporation of a laboratory sample after purification is used by the EPA to measure ^{228}Ac in the analysis for ^{228}Ra (EPA, 1984a), and sources of thorium, isolated from marine carbonates, have been prepared by evaporation for measurement by alpha spectrometry (Blanchard et al., 1967). Measured count rates of identified radionuclides, for which absorption curves have been prepared, can be adjusted for self absorption in evaporated test sources.

In the case of all dry sources, steps should be taken to prevent solids from exiting the planchet, which will affect the measurement and, in time, contaminate the detector. Sources consisting of loose, dry material, or with a tendency to flake, should be covered with thin plastic or immobilized by evaporating a few drops of a lucite-acetone solution on the solid deposit (PHS, 1967, p. 21).

16.7.4 Thermal Volatilization/Sublimation

Vacuum thermal volatilization or sublimation are often used when very thin and uniform sources are required (Blanchard et al., 1957, p. 7-9 and Friedlander and Kennedy, 1955, p. 122). The disadvantages of this technique are that it is time consuming and the recoveries are often less than 50 percent (NAS/NRC 1962, pp. 126-127).

The apparatus used to perform this procedure consists of a demountable vacuum chamber that contains either a ribbon filament, often with a shallow trough, or a crucible. The collector plate is usually mounted less than an inch away. The source solution is first evaporated onto the filament. As the required temperature of the filament is reached, the trough in the filament tends to collimate the sublimed material onto the collecting plate, increasing the recovery of the sample.

Pate and Yaffe (1956) designed a system for volatilizing radionuclides from a crucible heated with electrical resistance wire. Their design resulted in nearly 100 percent yields on thin collecting films, and made it possible to prepare thin and uniform sources containing a known aliquant of a stock solution (NAS/NRC 1962, p. 127).

For very thin sources, it is necessary either to swing the collector plate away or have it covered during initial heating in order to burn off impurities at low temperatures without volatilizing them onto the source mount. Separation from contaminants can be accomplished at the time of source preparation by considering differences in vapor pressure and carefully controlling the temperature (Coomber 1975, p. 306). The temperature at which a radionuclide will volatilize depends on the compound in which it exists, e.g., as a hydride, oxide, or halide. Sources have been prepared by thermal volatilization/sublimation for radioisotopes of manganese, chromium, cobalt, rhodium, arsenic, silver, ruthenium, technetium, and many others (Blanchard et al., 1957, p. 9; Coomber 1975, pp. 306-308). See Section 13.5, Volatilization and Distillation, for further discussion of this topic with examples.

A technique called vacuum evaporation has been used to prepare thin, uniform radioactive sources (Van der Eijk, 1973). Radioactive substances are volatilized by heating a solution in an oven under reduced pressure. Yields, usually rather low, can be improved by using a collimating oven.

16.7.5 Preparing Sources to Measure Radioactive Gases

Gaseous radionuclides most often measured include tritium, both as a vapor (^{3}HOH) and in the elemental form (^{3}H-H), ^{14}C, as CO_2, and the noble gases, ^{37}Ar, ^{41}Ar, ^{85}Kr, ^{131m}Xe, and ^{133}Xe.

Tritiated water vapor is often collected by condensation from a known volume of air (EPA 1984b). The air is drawn first through a filter to remove all particulates and then through a cold trap submerged in a dry ice/alcohol bath. A measured aliquant of the water collected is analyzed by liquid scintillation spectrometry (EPA, 1984b). Tritiated water vapor is sometimes collected by pulling air through a trap containing silica gel (SC&A, 1994). After collection, the water is distilled from the silica gel, collected, and counted in a liquid scintillation spectrometer.

Gaseous products of oxidation or combustion can be trapped in a suitable media, such as water for ^{3}H, ethanolamine for ^{14}C, peroxide for ^{35}S, and then analyzed by liquid scintillation spectrometry (NCRP, 1978, p. 211). For this method, it is very important to de-aerate the liquid prior to introducing the gas, and the temperature must be carefully controlled since gas solubilities are temperature dependent (NCRP, 1978, p. 210), generally inversely proportional to the temperature.

Although not as common nor convenient as liquid scintillation spectrometry, a gaseous radionuclide can be measured in an internal proportional counter as a component of the counter-filling gaseous mixture, usually argon, methane, or an argon-methane mixture (Friedlander and

Kennedy 1955, p. 274; NAS/NRC 1962, p. 128; Bleuler and Goldsmith 1952). For example, tritiated water can be reduced to hydrogen gas ($^3H_2$) by passing water vapor over a bed of hot zinc, and sodium carbonate can be converted to carbon dioxide ($^{14}CO_2$) by the action of an acid (NCRP, 1978, p. 211). These gases then can be mixed with a counting gas and introduced into the proportional-counter chamber. The major disadvantage of this technique is that it requires a gas handling system.

Concentrations of radioactive noble gases in the effluents of some nuclear facilities are sufficiently high that source preparation simply involves filling an evacuated vessel with the gaseous sample or flushing the vessel sufficiently to insure a 100 percent exchange (EPA, 1984b, pp. 19-20). The counting geometries (efficiencies) of the collection vessels can be determined, allowing the collected test sources to be measured directly in the vessels by gamma-ray spectrometry.

For environmental samples collected downwind of a nuclear facility, concentrating the nuclides in the gaseous sample is nearly always required prior to measurement. One example is a system, called the "Penn State Noble Gas Monitor," which was designed to measure low concentrations of radioactive noble gases (Jabs and Jester, 1976; Jester and Hepburn, 1977). Samples of environmental air are compressed in SCUBA (high pressure) bottles to 3,000 psig, providing a sample volume of 2.3 m^3. The inlet air to the compressor passes through a scrubbing train that contains particulate filters and activated charcoal to remove radioiodine. The noble-gas measurement system consists of a spherical 14.69 L, high-pressure, stainless steel vessel with a reentrant well in its base to permit insertion of a Ge detector connected to a spectrometry system. The vessel is surrounded with 2 inches of lead shielding.

There may be occasions when radioiodine is discharged into the atmosphere in several chemical forms. A molecular species filtering system, described by EPA (1990), collects four primary species of iodine on separate cartridges so that they can be measured individually. Air is pulled first through a particulate filter and then through the cartridges placed in series. The normal order of the four cartridges in the filtering system is as follows: (1) cadmium iodide media (CdI_2) for I_2 retention, (2) 4-iodophenol ($I \cdot C_6H_4 \cdot OH$) on alumina for HOI retention, (3) silver-salt (AgX) loaded zeolite or impregnated charcoal for organic iodine retention, and (4) charcoal for a breakthrough monitor. Air, at a calibrated flow, is passed through the system at a rate of one to two cubic feet per minute (cfm). When the sample-collection period is complete, the cartridges are separated, and the activities of each are measured separately by direct counting of the individual cartridges using gamma-ray spectrometry.

16.7.6 Preparing Air Filters for Counting

Air filters containing particulates may be counted directly by a proportional or scintillation detector. Minimal source preparation is normally required for directly counted filters. Some project plans may require that the mass of the particulates on filters be determined. If so required, the filters are weighed on receipt and the net particulate mass calculated by subtracting the mass of an average filter mass or, if pre-weighed, the beginning filter mass.

Actual preparation may be limited to a reduction of the size of the filter and placing it in the appropriate counting container, e.g., a planchet. If the filter is of the correct size and shape to fit directly in a counting container, no preparation may be required. Since particulate matter is deposited on the surface of the filter medium, care must be exercised in handling, particularly during size reduction, so that particulate material is not removed.

Because potentially contaminated material is relatively easily removed from a filter surface, caution is necessary to avoid contamination of detectors. If a filter is to be gamma counted it can remain in the envelope or plastic bag in which it is received for counting. The filter may be placed in such an enclosure if not received in that manner. The size of the filter may be reduced by simply folding the filter to a standard size for gamma counting.

When specific alpha- and beta-emitting nuclide analyses are required (e.g., Pu, U, Th, Am, Sr), the filter media along with the particulate material are usually ashed or dissolved and processed as any digestate by the procedure used in the laboratory.

16.7.7 Preparing Swipes/Smears for Counting

Swipes are collected to determine the level of removable surface contamination. They are normally taken on a filter paper or fabric pad by rubbing it over a predetermined surface area, nominally 100 cm^2. Swipes are routinely counted directly in a proportional counter for alpha and beta activity determination. The size of the swipe is selected to allow it to be placed in a standard-size planchet for counting. If elevated beta radioactivity is identified, a swipe may be gamma counted to determine the contributing radionuclide. Elevated alpha activity may require isotopic analyses for identification.

The precaution relative to detector contamination given above for air filters applies to swipes. All swipes should be treated as if they are contaminated until proven otherwise. In some cases swipes may be wetted with water or alcohol prior to collection of the sample. Wet swipes shall be

allowed to air dry prior to counting in order to avoid the reduction of particles reaching the detector due to absorption in the liquid remaining on the swipe.

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17 DATA ACQUISITION, REDUCTION, AND REPORTING

17.1 Introduction

This chapter provides information and guidance, primarily for laboratory personnel, on data acquisition, reduction, and reporting. Its intent is to provide an understanding of the many operational parameters which should be addressed in order that the data developed and reported are compliant with project planning documents (Chapter 4), considered valid (Chapter 8), and usable for their intended purposes (Chapter 9). These processes are all linked and each is dependent upon the results of its predecessor. The material presented is intended to provide an overview of the processes which are required in all radiochemistry laboratories, but are by no means performed in the same way in all laboratories.

In this chapter, data acquisition refers to the results produced by the radiation detection process, often referred to as counting. This chapter will provide guidance for laboratory personnel on selecting and applying the operational parameters related to instrumentation and the determination of the radioactivity contained in the test source.[1] Parameters that are applicable to counting for essentially all radiation detection instrumentation are discussed in Section 17.2 and those that are specific to a given type of instrumentation are covered in the appropriate section describing that instrument. A detailed description of the instrumentation discussed in this chapter was provided in Chapter 15.

Once test sources have been prepared (Chapter 16) and counted using laboratory measurement instruments (Chapter 15), the basic information generated by the instrument should be reduced (processed) to produce data which can be reviewed, verified, validated, and interpreted in light of and in accordance with project planning documents and analytical statements of work (SOWs) (Chapter 7). Data reduction is primarily mathematical in nature while data reporting involves the presentation of the results of the data acquisition and reduction processes and nonmathematical information necessary to interpret the data (e.g., sample identification and method of analysis).

Data reduction may be as simple as a division of the counts by the counting time, the sample aliquant weight or volume, and the counter efficiency, thereby producing the radionuclide concentration. On the other hand, it may also require more complicated processing such as the fitting of an analytical function, or the unfolding of a differential spectrum (Tsoulfanidis, 1983,

[1] The term "test source" will be used to describe the radioactive material prepared to be introduced into a measurement instrument and "laboratory sample" will be used to identify the material collected for analysis. Thus, a test source is prepared from laboratory sample material for the purpose of determining its radioactive constituents. "Calibration source" is used to indicate that the prepared source is for the purpose of calibrating instruments.

p. 327). In any case, the reduction process should continue by calculating the combined standard uncertainty (Chapter 19).

The output of some laboratory instruments is highly simplistic and consists only of the number of nuclear decay events recorded by the detector in the time interval allocated for the measurement. An example of this might be a gas-proportional counter whose only output is an electronic scaler and the available data consists of total counts or counts per minute. On the other extreme, some laboratory counting instruments with computer components produce outputs consisting of radionuclide concentration, uncertainty, and other information (see Chapter 19). Examples of these types of data reducing instruments are alpha- and gamma-spectrometry and liquid-scintillation systems.

ANSI N42.23 contains an outline of a minimal data report. Most project-specific planning documents (Chapter 4) and/or analytical SOWs (Chapter 5) require that the radiochemical data produced by laboratories be submitted in a specific format and form (i.e. electronic or hard copy, or both). In some cases, the requirements are minimal and may consist of a data report which gives only the sample identifier information, accompanied by the radionuclide concentration and its associated uncertainty. Many projects require much more supporting information, primarily to assist in the data validation (Chapter 8) process. Support material can include information on calibration, background determination, sample processing, sample receipt, quality control sample performance, raw-counting data, and chain-of-custody records.

This chapter gives an overview of data acquisition, reduction, and reporting in radiochemical laboratories. The material presented is intended to be descriptive rather than prescriptive, since these processes vary greatly between laboratories; depending upon the equipment, personnel, project requirements, and the methods and analyses being performed.

17.2 Data Acquisition

Data acquisition refers to the process of collecting the basic information produced by nuclear counting instruments. These data may be produced in hard copy or electronic format, or visually displayed for the operator to record. As previously stated, this can be simply the number of counts detected by the instrument within the allotted counting time or as conclusive as the identification of the radionuclides contained in the sample along with their concentrations and associated uncertainties.

Following generation, data requiring further processing may be electronically or manually transferred to the next to the next data-reduction step. Electronic transfer should be employed as

often as possible to avoid the inherent errors associated with manual transfer. On the other hand, the next step in the data reduction process may be performed manually, i.e., with a calculator.

The reliability of the data generated also depends upon the proper operation of the instrumentation and the associated data reduction programs. Data quality further depends upon the correct input of associated information by laboratory personnel.

17.2.1 Generic Counting Parameter Selection

Instrument operators have choices, provided by instrument manufacturers, in the setup and operation of nuclear counting instruments. These selections can affect the quality and applicability of the data. Some selections can be made on a one-time basis and left unadjusted for the processing of all samples and others require the operator to reevaluate the settings, possibly for each test source counted. In some cases adjustments can be made following counting during the processing of the derived information. Some adjustments can only be made before counting or by extending the counting time. In making the proper selection, there are some overall considerations relative to the project requirements, as specified in project planning documents (Chapter 4) or in the analytical SOW (Chapter 5). Other operator decisions depend on the nature of the test source itself. Caution should be exercised when changing operational parameters so that the calibrations (counting efficiency, energy, self absorption, etc.) performed on the instrument remain valid. For example, changing the source container or holder may affect the counting efficiency and/or background. Determining the appropriate operating conditions requires that the operator have a thorough understanding of the counting process and the instruments and their operation for the production of valid and useable data. In addition, the operator should be cognizant of the measurement quality objectives (MQOs) that have been established.

Some of the factors that affect operational parameter selection are related to project requirements. Planning documents and the analytical SOW may specify the limits on measurement uncertainty and detection capability. In order to achieve compliance with the limits, instrument operating parameter adjustment may be required for some or all the samples received. The number of samples received during a time period may make it mandatory for adjustments to be made in order to meet these requirements while complying with project defined turn-around-times.

Factors that may affect the selection of operational parameters include:

- Project and External
  - project requirements for uncertainty, detection capability, and quantification capability

- laboratory backlog and contract turn-around times

- Sample Characteristics
  - expected sample radionuclide concentration
  - interfering radionuclides
  - interfering stable constituents (e.g. liquid scintillation counting quenching)
  - amount of sample available
  - physical characteristics of the test source (e.g. density)
  - half-life of the radionuclide of interest

- Analytical Process
  - chemical separation process leading to counting source generation (Chapter 14)

- Instrumentation
  - instrument adjustments available and their limits
  - conditions and limits of an instrument's calibration
  - time availability of instruments
  - counting efficiency
  - calibration geometries available

Taking into consideration the above, the operator has control over and should select certain parameters for all radiation measurements. The selection of the basic parameters should be carefully planned in advance to assure that the project requirements are met. The laboratory's selection of parameters during the planning process may require alteration as the process of sample analysis is actually taking place due to unavoidable changes in the samples and sample characteristics throughout the duration of the study.

17.2.1.1 Counting Duration

For the Poisson counting model, the uncertainty associated with a given count determination is proportional to the square root of the total number of counts accumulated (Chapter 19). The total counts accumulated during counting are proportional to the activity of the source and the length of the counting time. Counting duration is a controllable factor that allows one to achieve a given level of counting uncertainty. The operator should then select a duration which is sufficient to meet project objectives for detection capability and uncertainty. The length of time allotted for determination of the instrument background will also affect the uncertainty associated with the measurement (Chapter 19). Thus, when preparing an analytical protocol to meet the requirements of a project, as expressed in the project planning documents, the laboratory will establish the

counting durations of both sample and background accordingly. An alternative to selecting a counting duration, available on many instruments, is to count until a preset number of counts is obtained.

17.2.1.2 Counting Geometry

The counting efficiency of a radiation detector depends on the geometry of the source and detector arrangement, e.g., the solid angle subtended at the detector by the source. A given radiation detector may have the counting efficiency established for several geometries. The geometry selected among those available may depend upon the amount of sample available, the detection capability required for the analysis, the radionuclide concentration in the sample, the dictates of the radioanalytical method, the physical characteristics of the sample, the nature and energy of the decay process, and the characteristics of the detector.

The choices to be made relative to geometry selection are usually the type of test source container, the source mounting, and the detector to source distance. Choices are to be made among those for which the detector has an established efficiency calibration.

17.2.1.3 Software

The use of properly developed and documented computer software programs for data acquisition and reduction can lead to an enhancement in the quality of laboratory data. Guidance on software documentation can be found in EPA (1995). Caution should be exercised in the selection and use of undocumented programs and those which may not have been tested in laboratories performing analyses similar to those for which MARLAP has been developed. For example, a spectral analysis program may accurately identify and quantify the radionuclides in test sources containing higher levels of radioactivity (which produce spectra with well defined peaks, easily distinguishable from background) but may be inaccurate for samples with environmental levels.

When selecting software, a thorough review of the data reduction algorithms should be performed. The user should not blindly accept the notion that all software performs the calculations in an appropriate manner without this review. When evaluating software, it is often helpful to review the software manual, particularly in regard to the algorithms used in the calculations. While it may not be necessary that the user understand in detail all the calculations performed by highly complex software programs, the user should understand the overall scheme of analysis and reduction in order to assure data meet quality objectives and reporting requirements. This understanding is also beneficial in assuring that user defined parameters are properly selected.

The output of some instruments is very basic, primarily counting data, i.e., counts or counts per second. These data should be manipulated by external systems to convert them to the form required by planning documents. The external system which performs the calculations may be a calculator or a computer with the appropriate software to reduce the data to usable terms. In either case, additional information relative to the processing of the sample should be input along with the counting data (counting time, total counts, and background counts). This information may include laboratory sample number, collection date, sample mass or volume, instrument counting efficiency, and chemical yield.

For computer (processor) based systems, some of this information is generated and processed internally and the remainder is manually entered or electronically transferred from the Laboratory Information Management System (LIMS) or some other adjunct system where it has previously been stored. It is becoming increasingly common for much or all of this adjunct information to be transferred to the counting instrument by reading a bar code affixed to the test source to be counted. In this manner, the information which has previously been entered into a LIMS is electronically transferred to the counting instrument. For hand calculations, these data are simply entered into the calculations.

17.2.2 Basic Data Reduction Calculations

The equations used for data reduction depend on the analytical methods used. The following equations are provided as examples to illustrate the basic principles involved in data reduction.

Following counting, the radionuclide concentration may be calculated:

$$R_C = \frac{C_{Net}}{\varepsilon \cdot V \cdot Y \cdot K_C \cdot e^{-\lambda t_1}} \qquad (17.1)$$

where:

R_C = radionuclide concentration at time of collection (Bq/L or Bq/g)
C_{net} = net count rate (cps)
ε = counter efficiency for the radionuclide (cps/dps)
V = volume or mass of sample analyzed (L or g)
Y = chemical yield (when appropriate)
e = base of natural logarithm
λ = the radioactive decay constant for the radionuclide (s^{-1}, min^{-1}, or d^{-1})

187 t_1 = time lapse from sample collections to beginning of source count (units consistent
188 with λ)
189 K_C = the correction for decay during counting and is:

$$K_C = \frac{1 - e^{-\lambda t_C}}{\lambda t_C} \tag{17.2}$$

190 where:
191 t_C = actual clock time (real time) of counting (units consistent with λ)

192 This calculates the radionuclide concentration at the time of sample collection[2]. It compensates
193 for the fact that short-lived radionuclides may experience significant reduction in activity during
194 counting, when the counting duration is a significant fraction of the half-life. For long-lived
195 radionuclides, the term K_C approaches unity and can be ignored. The efficiency used in this
196 equation may be obtained from the specific radionuclide whose concentration, R_C, is to be
197 determined or it may be obtained from an efficiency curve which plots counter efficiency vs.
198 energy. In the latter case, the abundance, E_e, of the particle or photon being counted should be
199 considered. This is required because the energy dependent efficiency, ε_e, is developed in terms of
200 the fraction of particles or photons detected divided by the number emitted at that energy. Thus,
201 if the radionuclide emission being determined during the counting of a test source has an
202 abundance less than 100 percent, an adjustment should be made to Equation 17.1, as shown in
203 Equation 17.3:

$$R_C = \frac{C_{Net}}{E_e \cdot \varepsilon_e \cdot V \cdot Y \cdot K_C \cdot e^{-\lambda t_1}} \tag{17.3}$$

204 Most modern instrument systems contain preprogrammed software to perform data manipula-
205 tions that convert basic counting information to a form which can be compared to the project data
206 quality objectives, or at least to begin or promote this process. Certain sample-specific
207 information should be manually entered or transferred to the system electronically in order to
208 perform the necessary calculations.

[2] For radionuclides with short half-lives detected at or near detection limits, it may be more appropriate to calculate the concentration at the time of counting.

17.3 Data Reduction on Spectrometry Systems

Software is available for resolving alpha, gamma, and liquid scintillation spectra and for performing the attendant functions such as calibration, energy alignment, background acquisition and subtraction, and quality control functions.

Spectroscopic analysis for alpha particles and gamma-rays is performed to identify and quantify radionuclides in samples. Since these emissions occur at discrete energies, spectrometry is useful for these purposes and can be applied to the analysis of a wide range of s radionuclides. Energy spectra are produced when a detector absorbs a particle or photon and produces a signal that is proportional to the energy absorbed. The resulting signal is digitized by an analog-to-digital converter and processed by a multichannel analyzer. A differential spectrum is produced, where the number of events within an incremental energy, ΔE, is recorded on the y axis and the energy is represented on the x axis (Tsoulfanidis, 1983, p. 327). In this way, radionuclides can be identified by the characteristic energies of their emissions and quantified because the area under the full energy peak is proportional to the emission rate (activity) of the source being analyzed.

The spectra for alpha and gamma emitters are quite different, due to the differences in the way these two types of radiation interact with matter in transferring their energy to the detector material. The process of resolving the spectra into its contributing components is referred to as spectral analysis (NCRP 1978, p. 159) and unfolding (Tsoulfanidis, 1983, p. 342). Computer programs for analyzing alpha and gamma spectra are available from several sources (Decker and Sandderson, 1992). A method of performance testing of gamma analysis software is given in ANSI N42.14.

17.3.1 Gamma Spectrometry

Gamma spectrometry on environmental samples requires the use of gamma spectral analysis software for any reasonable degree of accuracy and detection capability. This is due to the potentially large number of photopeaks to resolve, the low level of radioactivity in most environmental samples, and the relatively low detection limits and stringent quality control requirements of most project-specific planning documents. Spectral analysis by manual techniques is only practical when the number of radionuclides is limited and the contributing isotopes are predictable. An example is the analysis of milk samples for gamma-emitting radionuclides, where the milk production process in the cow restricts the number of radionuclides in the milk product (Hagee et al., 1960, p. 36; USPHS, 1967, pp. 1–51).

Gamma-rays interact with matter in three ways, namely, by photoelectric effect, Compton scattering, and pair production (Tsoulfanidis, 1983, pp. 141–148). These interactions within a gamma detector, usually a high-purity germanium or sodium iodide (see Chapter 16), result in varying amounts of the gamma-ray energy being absorbed. Only one of these interactions, the photoelectric effect, results in the total energy being absorbed in a single interaction. The photopeak, shown in Figure 17.1, due to a photoelectric interaction in the detector, results from the processing of the detector signal through the linear circuitry and the multichannel analyzer.

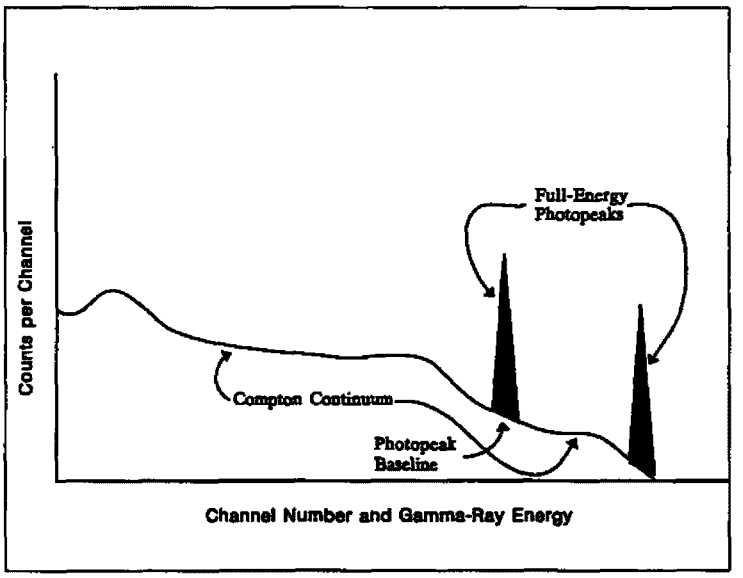

FIGURE 17.1 — Gamma-ray spectrum

This photopeak has a basic Gaussian shape (Gilmore and Hemmingway, 1995, p.163) and may be described by (Quittner, 1972, p.20):

$$y(x) = A\,e^{-(x-p)^2/2\sigma^2} \tag{17.4}$$

where:

A = the peak amplitude
x = the channel number
p = the peak centroid

(The width of the peak is related to the full-width at half-maximum (FWHM) of the detector, Γ, where $\Gamma = 2.355\ \sigma$. The area under the peak is $N = 1.064\ A\ \Gamma$.)

As can be seen in Figure 17.1, the photopeak (P1) may be displaced upward by its position on the Compton continuum from other, higher-energy gamma-rays (P2) and background radiation.

The photopeak is the key element in gamma-ray spectrometry in that its location on the energy axis provides a means for radionuclide identification, and the area under the peak is proportional

to the number of gamma-ray events comprising the photopeak. This becomes the basis for radionuclide identification and quantification.

The fundamental purposes of gamma-ray computer-based spectral analysis programs are to identify the photopeaks in a spectrum and to measure the true area under the photopeaks. It should do this in the presence of natural background, a potentially large number of sometimes overlapping photopeaks, and a great number of Compton-scattering events. Once these initial tasks have been performed, the computer program uses this information to determine the radionuclide mix that contributed the complex spectrum and the individual concentrations in the sample being analyzed.

Most computer programs for gamma-spectral analysis are provided by equipment manufacturers, although some are supplied by independent providers. There are significant differences in the structure of the programs. However, they all perform similar functions which are given below and illustrated in Figure 17.2.

17.3.1.1 Peak Search or Identification

There are two basic methods of gamma spectral analysis. The first method is to allow the analysis software to determine the existence of the peaks and their energy. The second method is often referred to as a "library directed" search, where the operator identifies the peak energy locations, e.g., regions of interest, to be searched for discernable peaks. The latter method may be more sensitive (Gilmore and Hemmingway, 1995, p.165) but, taken alone, will fail to identify and report unspecified radionuclides. If the confirmation of the existence of a particular radionuclide is required, the second method should be employed. Most software programs allow either approach to be activated and used for each analysis.

A most important function performed by an analysis program is the identification of true photopeaks. In the programs available, this is achieved in one of the four ways discussed below.

Many spectral analysis programs allow the operator to select among two or more of the four methods for peak identification. Selection of the most accurate and sensitive method depends on the radionuclides present in the source, detection capability requirements for individual radionuclides, the number of radionuclides present, the nature of the background spectrum, the degree to which the radionuclide mix can be predicted, and the activities of the isotopes. The selection of a particular peak search method can be determined by experience with similar sample types and past performance, particularly on performance evaluation (known) samples.

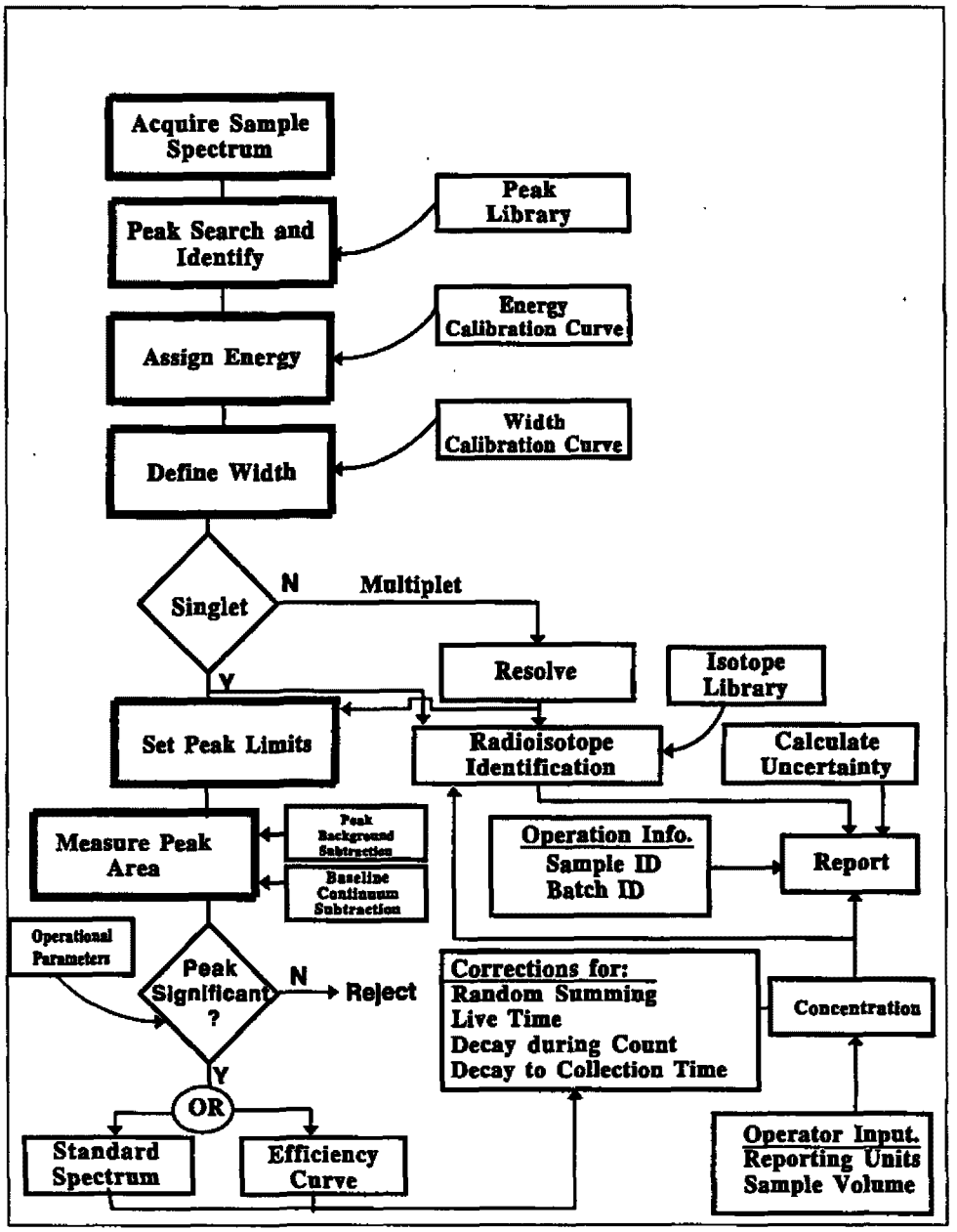

FIGURE 17.2 — Gamma-ray analysis sequence

301 REGIONS OF INTEREST (ROI) METHOD

302 This is the simplest form of peak identification, but can only be used when the radionuclides

present in the sample are known and when the analysis system has been compensated for gain drift. ROI analysis involves the establishment of predetermined energy regions, at least one for each radionuclide present. Once the spectrum has been acquired, the number of counts in each region is summed after subtracting the photopeak baseline (Figure 17.1). This method of spectral analysis is more applicable to alpha rather than gamma spectrometry.

GAUSSIAN FUNCTION DERIVATIVE METHOD

As previously stated, the photopeak has a basic Gaussian shape; in reality it is a histogram with a Gaussian-like shape. The most widely used peak identification technique was proposed by Mariscotti (Mariscotti 1967, p. 309) and uses the Gaussian function derivative to assess the presence of a photopeak. For most low-level radioactivity, this peak search method may provide the best peak detection capability with the fewest false peak identifications or omissions of true peaks (Gilmore and Hemmingway, 1995, p. 20).

CHANNEL DIFFERENTIAL METHOD

This method searches for a number of channels where the counts are significantly greater than the preceding channels, and then looks for the expected decrease in counts corresponding to the backside of the prospective photopeak. This method works relatively well for large, well-defined peaks, but is limited for poorly defined peaks with counts barely above the background baseline of the peak (Gilmore and Hemmingway, 1995, p. 163).

CORRELATION METHOD

In this method, a search function is scanned across the spectrum. Each channel count, over the width of the search function, is multiplied by the corresponding value of the search function. The sum of these products is then made a point on a correlation spectrum. A correction for the baseline contribution leaves only positive counts within a photopeak. Although the scan function is normally Gaussian in form, other forms may be applied (Gilmore and Hemmingway, 1995, p. 164).

Spectral analysis programs usually have some user selected peak acceptance criteria. The acceptance criteria may be based on peak shape, width uncertainty, or the number of standard deviations above the background to be subtracted. Care is required in selection of the values for these acceptance criteria. If the values are too high, valid photopeaks remain undetected. If the values selected are too low, radionuclides may be reported which are not present in the samples. Knowledge of the sample origin and experience with using the analysis program on similar

samples to those being processed is useful in establishing values for these user-selected parameters. Peak searches may be standard or directed (Canberra, 1994). In a standard search, all peaks identified are assigned to a library contained radionuclide. In a directed search, the user specifies the energies and radionuclides over which the search is performed. If reporting of a specific radionuclide is required, the directed search is appropriate; however, some radionuclides could go unreported if only a directed search is performed.

17.3.1.2 Singlet/Multiplet Peaks

A peak is referred to as a singlet or multiplet according to whether it is composed of a single photopeak or multiple photopeaks, respectively. Deconvolution is the term given to the process of resolving a multiplet into its components (Gilmore and Hemmingway, 1995, p. 172). The ability of a spectral analysis program to perform this function may well be the deciding point for its selection. It is particularly important if the laboratory has analyses in which one of the critical radionuclides has only one gamma-ray whose energy is very near to that of another radionuclide expected to be present in all or most samples.

There are three primary ways that programs deal with the problem of resolving multiplets. The first method is a deconvolution algorithm which is based on the peak-shape being the composite of multiplet Gaussian distributions. The second method uses the gamma-ray library to anticipate where peaks occur within a multiplet. The disadvantage of the first is in dealing with small ill-defined peaks and the second cannot, of course, resolve peaks not included in the library. The third method, peak stripping, again depends on defining all radionuclides whose gamma-rays contribute to the multiplet. In peak stripping, one of the interfering gamma-ray's contribution is subtracted from the multiplet area by using another of its gamma-rays to estimate the peak shape and size in the multiplet area. The remaining peak is, presumably, that of the interfered radionuclide which can then be identified and quantified. This method requires that one of the interfering radionuclides have a second gamma emission which identifies and tentatively, for the purpose of removing its contribution, quantifies it.

In some cases, the uncertainty of multiplet deconvolution can be avoided by selecting photopeaks from gamma-rays which are not interfered with, even though they may have lower abundances. The increase in uncertainty due to the lower number of accumulated counts may well overcome the uncertainty of deconvolution (Gilmore and Hemmingway, 1995, p. 174).

364 17.3.1.3 Definition of Peak Centroid and Energy

365 Once a peak has been detected, the centroid of the peak will be defined, since it will rarely be
366 located at exactly a whole channel number. The centroid will be used to represent the gamma-ray
367 energy and should be calculated to the fraction of a channel. An algorithm is used to calculate the
368 centroid value may be expressed as (Gilmore and Hemmingway, 1995, p. 167):

$$\text{Centroid} = \frac{\sum C_i i}{\sum C_i} \tag{17.5}$$

369 where:
370 C_i is the count in the i^{th} channel.

371 In order to assign a gamma-ray energy value to the peak centroid channel position, the analysis
372 program refers to a previously established energy calibration file. The detector's response to the
373 full range of gamma energies should be established by counting a source(s) having a number of
374 well-defined gamma-rays over the range of energies emitted by the radionuclides in the
375 calibration source. This calibration source is most often a "mixed-nuclide source," which also
376 has certified emission rates so that it may also be used for an efficiency calibration. The mixed-
377 nuclide source is counted on the detector, being sure to accumulate sufficient counts in the peaks
378 to obtain good statistical precision, and an energy-versus-channel relationship is established. The
379 operator will be required to provide information on the peaks to be used and their exact energies.

380 With modern spectrometry systems, the relationship between energy and channel number is
381 nearly linear. Both linear and quadratic fits have been included in available spectral analysis
382 programs.

383 17.3.1.4 Peak Width Determination

384 In order to calculate the area under the peak, an estimate of the peak width is required, unless the
385 analysis program is operating in the region-of-interest mode. The width of a photopeak is
386 normally quoted in terms of its FWHM. For a discussion of peak width (resolution) and the
387 factors affecting it, see Chapter 15.

388 There are several ways to determine the peak boundary. These are:

389 (1) A Gaussian shape is assumed and some number of standard deviations (2 or 3) are
390 allowed on each side of the peak centroid.

(2) A standard width for each peak, based on its energy, is used.

(3) A five-point moving average is used to determine a minimum on each side of the peak, which is set as the peak limits.

Each method has strengths and weaknesses, but all struggle with ill-defined (small number of counts) peaks. Once the peak limits are defined, determining the area under the peak is accomplished by summing the counts per channel for the channels contained in the peak and subtracting the baseline (see Figure 17.1).

The determination of FWHM requires an assumption of peak shape and, as has previously been stated, the acceptance of a Gaussian function is the norm for gamma spectrometry. In addition, the peak width increases with the energy of the gamma-ray, so some function should be defined for the analysis program to determine the width based on the energy of the peak. This relationship, in practice, is found to be nearly linear (Gilmore and Hemmingway, 1995, p. 133) and described by:

$$w = a + bE \tag{17.6}$$

where:

w = width of the peak
E = the energy
a, b = empirical constants

For spectra developed by high-purity germanium semiconductors (HPGe) and alpha solid state detectors, it is more appropriate to assume a peak shape which is a modification of the Gaussian function to allow for the low energy tailing observed in these spectra. This type of tailing is illustrated in Figure 17.3. Some spectroscopy programs have algorithms to fit peaks with lower energy tailing.

When the "tailing" peak fit option is selected, the software algorithm for peak fitting changes from the pure Gaussian form to a dual fit. The channels in the peak not affected by the tailing are included in the Gaussian fit (Equation 17.7), and those that are affected by tailing are modified according to Equation 17.8, below:

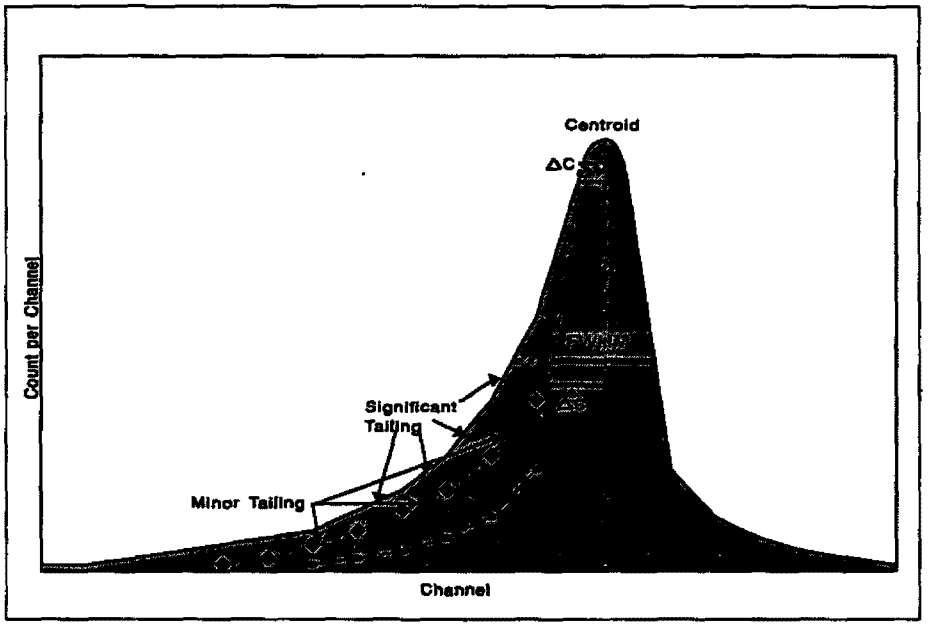

FIGURE 17.3 — Low-energy tailing

$$y(x) = \begin{cases} Ae^{\frac{-(x-P_C)^2}{2\sigma^2}}, & x \geq P_C - \Delta C \quad (17.7) \\ Ae^{\frac{\Delta C(2x-2P_C+\Delta C)}{2\sigma^2}}, & x < P_C - \Delta C \quad (17.8) \end{cases}$$

where:

- x = the channel number
- A = the peak amplitude
- P_C = the peak centroid
- ΔC = the tailing factor (the distance from the centriod to the point where the tailing joins the Gaussian peak)
- σ = the width of the Gaussian peak ($\approx 2.355 \times$ FWHM)

424 17.3.1.5 Peak Area Determination

425 For single peaks sitting on a Compton continuum, two methods of peak area determination are
426 available. The simpler method is the addition (integration) of the number of counts per channel in
427 each of the channels considered to be within the peak limits, and subtracting the natural
428 background and Compton contribution to those same channels (Baedecker, 1971; Loska, 1988).
429 However, this is rarely simple since the photopeak is usually offset by a baseline continuum
430 whose contribution is not easily determined. While the background may be subtracted by the
431 spectrometry program, the Compton continuum will be estimated by the software and then
432 subtracted. This estimation is often based on the number of counts per channel in those channels
433 immediately above and below the photopeak region as shown in Figure 17.4.

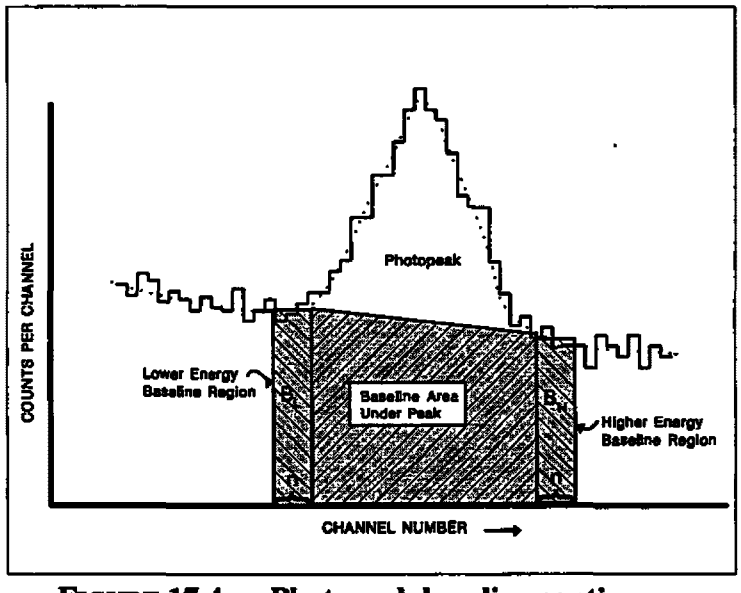

FIGURE 17.4 — Photopeak baseline continuum

434 The baseline contribution is then estimated as:

$$B = \frac{N}{2n}(B_L + B_H) \qquad (17.10)$$

435 where:
436 B = the number of counts attributed to the baseline
437 N = number of channels in the peak

438 n = the number of baseline channels considered on each side of the peak for calculating
439 B_L and B_H
440 B_L = the sum of the number of counts in the baseline region on the low-energy side
441 B_H = the sum of the number of counts in the baseline region on the high-energy side

442 In practice, the baseline continuum appears to have a step beneath the peak (Gilmore and
443 Hemmingway, 1995, p.114), as illustrated in Figure 17.5. This type of function is estimated by:

$$B = \sum_{i=1}^{N} \left[\frac{B_L}{n} + \frac{B_H - B_L}{nG} \sum_{j=1}^{i} y_j \right] \tag{17.11}$$

444 where:
445 B_L = sum of counts in the baseline region on the low-energy side
446 B_H = sum of counts in the baseline region on the high-energy side
447 y_j = counts per channel in channel j
448 G = gross counts in the peak
449 N = number of channels in the peak
450 n = number of channels in each of the two baseline regions

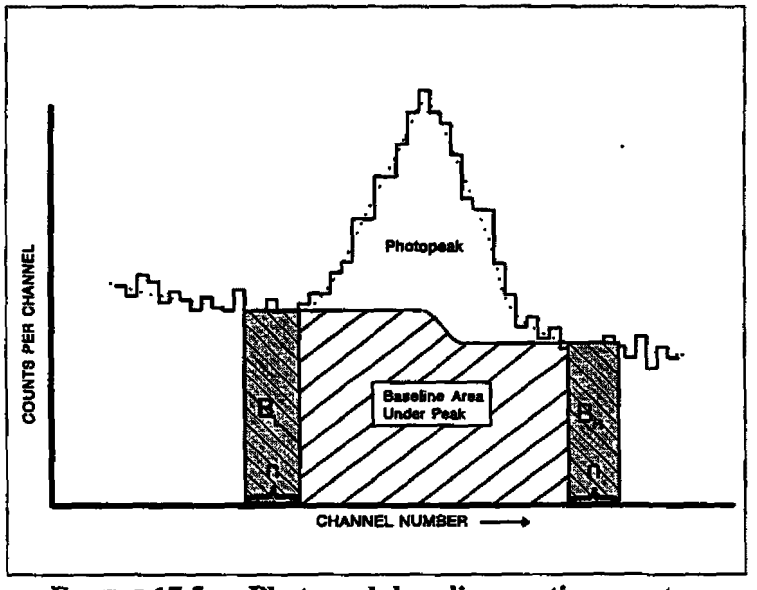

FIGURE 17.5 — Photopeak baseline continuum-step function

The second peak area determination method is the least-squares method, which fits a theoretical peak shape plus background shape to the channels surrounding the peak (Kruse and Spettel, 1982; Helmer et al., 1983). Background is often subtracted prior to the fitting process (Loska and Ptasinski, 1994).

17.3.1.6 Calibration Reference File

Three types of calibrations are required for gamma spectral analysis, namely those for efficiency, energy, and FWHM. Efficiency and energy calibrations require a source whose gamma-ray emission rate is known and referenced to a national standard, and whose gamma-ray energy lines are well known. "Mixed radionuclide" reference material, containing eight or more gamma lines, is available for performing these spectral calibrations. The operator is required to enter the pertinent information, usually listed in the calibration source certificate, into the file prior to performing the calibrations. The information generally consists of:

- Radionuclide name;
- Certified activity and units;
- Uncertainty in activity;
- Reference date and time;
- Gamma energies and branching ratios; and
- Half-life.

Once calibration files are established, the calibrations are performed according to methods specific to individual software and as described in manufacturers manuals (also see Chapter 16).

17.3.1.7 Activity and Concentration

In order to convert the counts under a photopeak to activity, an efficiency calibration should be performed on the detector. Since the efficiency varies with energy, the detector should be calibrated over the range of energies to be used and a calibration curve developed for the detector. In constructing an efficiency calibration curve, only calibration sources with singlet peaks and well-known abundances should be selected. The efficiency, at a specific energy, is simply the number of counts determined in a photopeak of known energy divided by the number of gamma-rays emitted by the source in the same time period, or:

$$\varepsilon = \frac{C_r}{D} \qquad (17.12)$$

where:

ε = efficiency in cps/γps
C_r = cps in the photopeak
D = gamma emission rate of source in dps

The efficiency versus energy curve developed in most gamma software packages is in the form of a polynomial. One such form is:

$$\ln \varepsilon = \sum_{i=0}^{n} b_i \cdot [\ln E]^i \qquad (17.13)$$

where:

ε = full peak efficiency
b_i = coefficient as determined by calculation
E = the energy of the photopeak

The efficiency curve for high-purity germanium detectors shows two distinctive slopes. The polynomial fit in some analysis programs allows for a dual fit, i.e., a separate fit is made to the two portions of the curve.

This efficiency curve is maintained in the calibration file of the spectral analysis program to be applied to each analysis. An efficiency curve should be maintained for each test-source geometry to be used for the calibrated detector.

To obtain the activity in the test source, the net counts (background subtracted) in the photopeak, as determined by the software through the process described above, is divided by the geometry-specific efficiency. The activity units are converted to those selected by the operator and corrected for decay to the time of collection. Based on sample-aliquant size/volume information supplied by the operator, sample concentration is calculated and reported.

17.3.1.8 Summing Considerations

Summing refers to the summing of the energy of two or more gamma-rays when they interact with the detector within the resolving time of the spectrometer's electronics. There are two types of summing: (1) *random summing*, where two unrelated gamma-rays are detected at the same time, and (2) *true coincidence summing*, is due to the simultaneous emission of gamma-rays by a radionuclide and their subsequent detection by the gamma detector.

Random summing, sometimes referred to as pile-up, is due to gamma-rays, from different radionuclides, being detected almost simultaneously. If two gamma-rays arrive at the detector within the resolving time of the amplifier and both have a photoelectric interaction, instead of having a count in both full-energy peaks a count will occur somewhere else in the spectrum equal to the sum of the two energies. Random summing can also occur with other than photoelectric interactions, e.g., photoelectric with Compton and Compton with Compton. Since this occurs randomly in nature, the probability of random summing increases with the square of the total count rate. Random summing can be reduced by the use of pile-up rejection circuitry which examines the pulse shape of detector signals and rejects those which are distorted by summing (Gilmore and Hemmingway, 1995). However, even with pile-up rejection random summing will still be present. A mathematical correction for random summing is given by:

$$A_T = A e^{2R\tau} \tag{17.14}$$

where:

A_T = the true peak area (counts)
A = the observed peak area (counts)
R = the mean (total) count rate (cps)
τ = the resolving time of the electronics (μs)

If unknown, the resolving time can be estimated by a method similar to that described in Gilmore (1995).

True coincidence summing is a source of error when a source contains nuclides which emit gamma-rays nearly simultaneously. Coincidence summing is geometry dependent and increases as the source is positioned closer to the detector. Thus, the use of multi-gamma-ray calibration sources for close geometry efficiency calibrations must be done with caution. True coincidence summing also increases with detector volume and is very prevalent in a well detector. The use of a detector with a thin entry window opens the possibility of coincidence summing with X-rays. Since coincidence summing is independent of count rate, it is a mistake to assume that the measurement of environmental media is immune from errors caused by this phenomena.

As is the case with random summing, true coincidence summing results in the loss of counts from photopeaks and a corresponding loss in efficiency. The use of single gamma-ray emitting radionuclides is recommended, to the extent possible, for developing calibration curves for detectors at close geometries. In practice, even when the efficiencies are determined in this manner, errors in analyzing for nuclides emitting more than one gamma-ray still exist. When a multi-emitting gamma-ray source is to be measured with minimum bias, it may be necessary to

perform an efficiency calibration with the specific radionuclide to be measured in the specific geometry desired.

In theory it is possible to mathematically correct for true coincidence summing; however, for complicated decay schemes, the task is daunting (Gilmore and Hemmingway, 1995). Some data have been published which give correction factors for coincidence summing for a number of radionuclides (Debertin and Helmer, 1988). Unfortunately they only apply to the particular detector and geometries for which they were developed.

17.3.1.9 Uncertainty Calculation

The various components of uncertainty in the determination of the source activity should be propagated to obtain the combined standard uncertainty. The sources of uncertainty in the gamma spectral analysis include those associated with the determination of the net peak area, which includes the standard uncertainties of the gross counts, the background counts, and any interference from other gamma radionuclides present; the uncertainty associated with the unfolding of multiplets; the detector efficiency, which includes uncertainties of the net peak area, the calibration source emission rate, and decay correction factor; and uncertainty in the determination of the sample volume or mass.

$$u_c = \sqrt{u_P^2 + u_V^2 + u_\varepsilon^2 + u_U^2} \tag{17.15}$$

where:

u_c = the combined standard uncertainty
u_P = the component of combined standard uncertainty due to the net peak area determination
u_V = the uncertainty component for the volume or mass determination
u_ε = the uncertainty component for the efficiency determination
u_U = the uncertainty component for the unfolding routine for multiplets

Each of these factors may have a number of components of uncertainties included, for example, the net peak uncertainty:

$$u_P = \sqrt{u_G^2 + u_B^2 + u_E^2 + u_I^2} \tag{17.16}$$

where:

u_G = the uncertainty component for the gross counts in the peak

565 u_B = the uncertainty component for the baseline subtraction
566 u_E = the uncertainty component for the background peak subtraction
567 u_I = the uncertainty component for the coincidence summing correction

568 The calculations of combined standard uncertainty typically are performed by the spectrometry
569 software for an alpha-spectrometry analysis. It should be noted that not every available software
570 package will incorporate all the listed uncertainty contributions listed.

571 **17.3.2 Alpha Spectrometry**

572 This section deals with alpha spectrum reduction as applied to semiconductor detectors, since it
573 is likely that this is the type of detector that will be employed for environmental analyses.

574 Since the range of alpha particles is a few centimeters in air and their energy is significantly
575 degraded in passing through a few millimeters of air, alpha spectrometry is conducted in a partial
576 vacuum and on extremely thin sources prepared by electrodeposition or coprecipitation (see
577 Chapter 16).

578 The number of full energy peaks is usually not large, three to four, in an alpha spectra and they
579 are normally well separated in energy. This, coupled with the fact that the test source subjected to
580 counting has gone through a chemical separation (Chapter 14), makes the radionuclide identifica-
581 tion relatively simple when compared to gamma spectrometry. However, it is still of great benefit
582 to have alpha spectrometry software to identify s.radionuclides, subtract background, perform
583 calibrations and energy alignments, determine radiochemical yields, and perform and track
584 quality control functions. In production laboratories where hundreds of alpha spectra may be
585 generated each week, it is almost imperative that alpha spectra are resolved by properly designed
586 computer software. An alpha spectrum produced by a semiconductor detector by the counting of
587 a thin source containing ^{234}U, ^{238}U, ^{239}Pu, and ^{241}Am is shown in Figure 17.6.

The spectrum demonstrated contains four peaks which are distorted from their basic Gaussian shape because each of the isotopes emits more than one alpha particle whose energies are within the resolving power of the detector and electronics. The FWHM of the peaks shown is approximately 30 keV. Of particular note is the fact that the peaks are essentially sitting on the baseline.

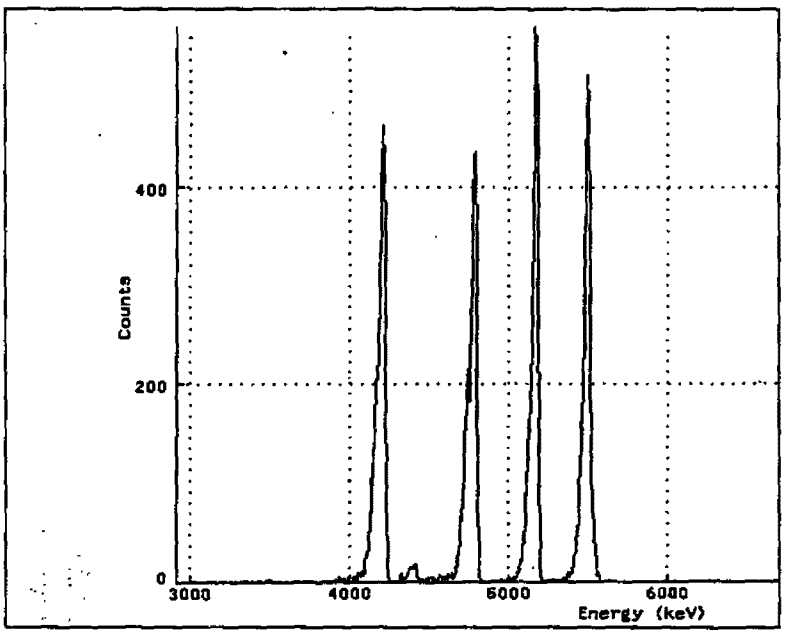

FIGURE 17.6 — Alpha spectrum

Spectral analysis programs usually have routines for the identification of full-energy peaks. However, in the case of alpha spectrometry, because the locations of peaks in the spectrum are known and the peaks may contain a small number of counts, an ROI-type of analysis is usually performed. However, peak fitting programs are available and may be beneficial when overlapping of peaks is possible. The algorithms used for peak fitting of alpha spectra should take into account the low energy tailing present in most alpha sources (Equation 17.8). The algorithms which account for tailing are modified Gaussian functions and require a peak shape calibration where a number of well-defined singlet peaks covering the full energy range are acquired. The calibration program then calculates the tail parameter values (see discussion on tailing in Section 17.3.1.4, "Gamma Spectrometry").

Alpha peaks are normally sitting on the baseline (no background continuum) and display minimal overlapping for well-prepared sources. For a given analysis (Pu, U, Am, Th, and etc.), ROIs are established for all energies of the alpha emissions in the source being counted and the count rate in a given ROI represents the emission rate of the alpha whose energy falls within that ROI.

Given these qualifications, the spectral analysis software performs essentially the same functions as that for gamma analysis, described above. The programs may also perform system control function, e.g., maintaining vacuum in the chambers. Databases related to procedures, chemical tracers, and efficiency and energy calibration standards are normally maintained for calculational,

documentation, and quality control purposes. The general analysis sequence for alpha spectrometry will be briefly discussed below.

An efficiency calibration is not an absolute necessity if a standard/reference material is used for a tracer in each sample and an accurate determination of the yield is not required. In some cases, the laboratory may perform an energy and efficiency calibration for an alpha spectrometry analysis. This requires the operator to establish a calibration certificate file for the program to reference. It should refer to this file for both energy and efficiency calibrations. Calibration sources are necessary for performing the required calibrations, and the appropriate certificate information should be entered into the certificate files in order to perform the calibrations and to analyze test sources. This information should be supplied with calibration sources. Calibration sources , consisting of three to four radionuclides, are available in the form of plated discs from several commercial suppliers.

Information typically required by the analysis program consists of the following:

- Radionuclide
- Activity
- Assay date
- Half-life
- Energy
- Energy uncertainty
- Emission probability per event
- Emission rate uncertainty
- Activity units

This information should be entered for each of the radionuclides included in the calibration source. Once the library file has been established, an energy calibration can be performed as directed by the software program.

The efficiency for alpha particles varies only slightly with energy, within the range of alpha energies usually encountered. While the calibration source may contain several certified radionuclides, during an efficiency calibration, the mean efficiency for the full-energy peaks may be calculated and used as the alpha efficiency for a given detector (Chapter 16).

Once the alpha spectrometry system has been calibrated and a spectrum of a test source acquired, either a peak search is performed to identify alpha peaks or, if operating in a ROI mode, the counts in the ROI are determined. ROIs to be used for a given analysis are established prior to the

spectrum acquisition by selecting an analysis protocol where the radionuclides and their alpha energies are preestablished.

In the ROI mode, the counts accumulated during the preset counting duration in each of the designated regions are corrected for background contribution and, in some cases, for reagent blank activity. If a tracer has been added to the test source, the counts in the tracer ROI are summed, background corrected, and the effective efficiency (yield times counting efficiency) determined using certificate information previously entered by the operator and/or from a protocol file. The yield, if required, is then computed by the use of an efficiency which has been previously determined during an efficiency calibration process. The radionuclide concentration is then calculated by[3]:

$$R_{C_i} = \frac{C_{R_i}}{\varepsilon_e \cdot V \cdot e^{-\lambda_i t_1}} \qquad (17.17)$$

where:

R_{C_i} = radionuclide concentration of the radionuclide at time of collection (Bq/L or Bq/g)
C_{R_i} = net count rate in the designated ROI for the radionuclide (cps)
ε_e = effective efficiency ($\varepsilon \cdot Y$) for the tracer (cps/dps)
V = volume or mass of sample analyzed (L or g)
e = base of natural logarithm
λ_i = the radioactive decay constant for the radionuclide (s^{-1}, min^{-1}, or d^{-1})
t_1 = time lapse from sample collection to beginning of source count (units consistent with λ_i)

Following the spectrum acquisition process, spectral analysis programs may either automatically process the data and present the results, or they may store the spectral data and await interaction from the operator for processing. In either case, post-acquisition review of the analysis results is recommended. This review may include the following items:

- Assure that the alpha peaks fall within the ROIs;
- Confirm the absence of unexpected peaks (contamination);
- Verify that there are no interfering peaks;
- Confirm that peak centroids are within requirements (energy alignment);
- Verify that all requirements are met with regard to FWHM and chemical yield; and

[3] For certain alpha-emitting radionuclides, ^{224}Ra for example, a decay-correcting term is needed.

682 • Check units and sample aliquant information.

683 The FWHM of a given peak may depend greatly on the source preparation. However, since an
684 ROI-type of peak search is normally used, and the limits of the peak determined by the setting of
685 the ROI rather than some algorithm, the peak width definition is not significantly affected by
686 reasonable peak broadening. As a precautionary measure, the above review of each test-source
687 spectrum assures that the peaks appear within the ROIs. Alpha spectrometry analysis software
688 allows for the adjustment of the ROIs to account for peak broadening and slight displacement. A
689 review of the FWHM of the alpha peaks, as calculated by the software, will also reveal peak
690 broadening due to matrix effects and poor test-source preparation.

691 17.3.2.1 Radiochemical Yield

692 Alpha spectrometry test sources are usually prepared by radiochemical separation and the
693 chemical recovery may be less than 100%. Therefore, a radiochemical tracer, which is an isotope
694 of the radioactive species for which the analysis is being performed, may be added to the sample
695 prior to preparation and radioanalysis. The tracer is normally a certified standard solution whose
696 recovered activity is determined during the alpha spectrometric analysis in the same manner as
697 the activities of the isotopes for which the analysis is being performed. The radiochemical yield
698 is then calculated by the spectral analysis program according to:

$$Y = \frac{A_R}{A_S} \tag{17.18}$$

699 where:
700 Y = radiochemical yield
701 A_R = calculated activity recovered
702 A_S = certified activity added (decay corrected to time of counting)

703 The calculation of the chemical yield is normally performed by the alpha spectrometry analysis
704 software using operator input information relative to the alpha energy and abundance, activity,
705 uncertainty, and date of certification of the radiochemical tracer.

706 For some types of radionuclide analyses, no suitable alpha-emitting radionuclide may be
707 available for use as a chemical yield tracer. In this case, the chemical yield may be determined by
708 some other method, such as beta counting, and the resulting yield value provided to the alpha
709 analysis program so the source activity may be calculated from the alpha spectrometry data.

When a reference material is used for the chemical tracer, the effective efficiency is measured for each test source. If the chemical yield is to be reported, an independent measure of the counting efficiency should be made.

17.3.2.2 Uncertainty Calculation

The calculation of the combined standard uncertainty for alpha spectrometry is similar to that for gamma-ray spectrometry as reported in Section 17.3.1.8 above. One additional source of uncertainty which should be taken into account for alpha spectrometry is that associated with the determination of radiochemical yield. Since a tracer is added to the sample and the yield determined by a counting process, the uncertainty involved in this analysis should be accounted for in the total uncertainty. The uncertainty of the yield determination involves that associated with the net count of the tracer, the counting efficiency, and that of the emission rate of the tracer material. The combined standard uncertainty of the radionuclide concentration, R_{C_i}, is given by either

$$u_c(R_{C_i}) = \sqrt{\frac{u^2(C_{R_i})}{\varepsilon_e^2 V^2 e^{-2\lambda_i t_1}} + R_{C_i}^2\left(\frac{u^2(V)}{V^2} + \frac{u^2(\varepsilon_e)}{\varepsilon_e^2}\right)} \qquad (17.19)$$

or

$$u_c(R_{C_i}) = \sqrt{\frac{u^2(C_{R_i})}{\varepsilon^2 Y^2 V^2 e^{-2\lambda_i t_1}} + R_{C_i}^2\left(\frac{u^2(V)}{V^2} + \frac{u^2(\varepsilon)}{\varepsilon^2} + \frac{u^2(Y)}{Y^2} + \frac{2u(\varepsilon, Y)}{\varepsilon \cdot Y}\right)} \qquad (17.20)$$

where:

- C_{R_i} = net count rate in the designated ROI for the radionuclide (cps)
- ε = the alpha counting efficiency
- Y = the chemical yield
- ε_e = effective efficiency ($\varepsilon \cdot Y$) for the tracer (cps/dps)
- V = volume or mass of sample analyzed (L or g)
- e = base of natural logarithm
- λ_i = the radioactive decay constant for the radionuclide (s^{-1}, min^{-1}, or d^{-1})
- t_1 = time lapse from sample collection to beginning of source count (units consistent with λ_i)
- $u(\cdot)$ denotes the standard uncertainty of a quantity
- $u(\cdot,\cdot)$ denotes the covariance of two quantities

The two uncertainty equations are equivalent. However, when the yield is determined using an alpha-emitting tracer, Equation 17.19 generally is easier to implement.

17.3.3 Liquid Scintillation Spectrometry

17.3.3.1 Overview of Liquid Scintillation Counting

All modern counters are computer controlled for data acquisition, spectral unfolding, data reduction, sample changer control, external quench correction, and performing the multifarious other functions associated with liquid scintillation counting.

Liquid scintillation has traditionally found its primary use in the analysis of low-energy beta emitters, such as ^{3}H and ^{14}C. In spite of the complicating factors of high background and quenching (Chapter 15), procedures for other beta- and alpha-emitting isotopes have been developed over the years (Holm, 1984; Harvey, 1970).

Liquid scintillation has also been applied to the simultaneous analysis of alpha and beta emitters in environmental media (Leyba, 1992). Discrimination between alpha and beta radiation is based on differences in the fluorescence decay pulses. Pulse height is proportional to particle energy, and high counting efficiency results from 4π (4-pi) geometry and the absence of test-source self-attenuation (McDowell and McDowell, 1993). Because of these characteristics, liquid scintillation counting can be utilized as an alternative to gas proportional counting (Section 17.4) and alpha semiconductor counting (Section 17.3.2).

17.3.3.2 Liquid Scintillation Spectra

The amount of light produced by alpha and beta particles in a liquid scintillation cocktail is proportional to the particle energy. Beta spectra convey the energy continuum from zero to their maximum energy. Alpha liquid scintillation spectra are similar in shape to those obtained by semiconductor spectroscopy, but with greatly decreased resolution. Because alpha particles are only about one-tenth as efficient as beta particles in producing scintillation light pulses, there is an overlap of alpha and beta spectra (Passo and Kessler, 1992; McDowell and McDowell, 1993).

Gamma radiation interactions within the scintillation cocktail depend on energy and path length, with lower energy gamma rays being more efficient in transferring their energy. Gamma events are recorded in the same energy range as alpha and beta particles; therefore, discrimination between alpha, beta, and gamma radiation based solely on scintillation spectra is not possible (Passo and Kessler 1992; McDowell and McDowell, 1993).

766 17.3.3.3 Pulse Characteristics

767 Excited triplet and singlet energy states are formed by the fluor molecules when ionizing
768 radiation interacts with the scintillation cocktail. The excited singlet states dissipate their energy
769 very rapidly and produce short lifetime decay pulses, whereas triplet states lose their energy more
770 slowly, resulting in longer lifetime pulses. Because alpha particles have a higher linear energy
771 transfer than gamma or beta radiation, they produce a higher ratio of triplet to singlet excitation
772 states and therefore have a longer pulse duration. Differences in the decay time and shape of the
773 decay pulse are the basis for discriminating of alpha particles from beta and gamma radiation in
774 liquid scintillation counting (Passo and Kessler 1992; Passo and Cook 1994).

775 17.3.3.4 Coincidence Circuitry

776 Most modern liquid scintillation counters employ two photomultiplier tubes 180 degrees apart
777 for the detection of pulses. The light produced when ionizing radiation in the test source interacts
778 with the scintillation cocktail is emitted in all directions. A sample event should therefore
779 produce electronic pulses in both photomultiplier tubes simultaneously, or in coincidence.

780 Electronic noise pulses are produced randomly by the photomultiplier tubes, but the probability
781 that both tubes will produce noise pulses simultaneously is very low. An electronic gate can be
782 set to allow only pulses that are in coincidence to be registered. The rejection of random pulses
783 keeps background counts produced by electronic noise to a minimum.

784 17.3.3.5 Quenching

785 Chemical quenching reduces the amount of energy transferred to the fluor molecules. Halogens,
786 water, solvents, and oxygen are common agents that cause a decrease in the counting efficiency.

787 Color quenching is caused by impurities not removed during test-source preparation or by carrier
788 compounds such as iron chloride. Photons emitted from the fluor molecules are absorbed,
789 reducing the amount of light reaching the photomultiplier tubes.

790 Quenching causes a shift in the scintillation spectrum to lower energies and a reduction in the
791 number of counts. Quenching has a minimal impact on alpha counting, but significantly increases
792 as the energy of the beta particle decreases.

793 The most common method for monitoring quench is through the analysis of the Compton
794 spectrum. After the test source is loaded into the counter, it is irradiated by an external gamma

emitting source located in the instrument. The test-source spectrum is collected and compared with factory or user-generated quench standards stored in the instrument library. Both color and chemical quenching cause a shift to lower energies, but the color quench broadens the spectrum as well. The efficiency of the test source is extrapolated and applied to normalize the test-source count rate.

17.3.3.6 Luminescence

Photoluminescence is produced by ultraviolet light from the environment reacting with the scintillation cocktail. The effect can be minimized by dark adapting the test sources prior to counting.

Chemiluminescence is produced by reactions between the scintillation cocktail and chemicals introduced from the test-source preparation. To minimize this effect, oxidizers and alkaline conditions should be avoided.

Both photoluminescence and chemiluminescence cause random scintillation events. At low levels, the coincidence gate should reject most of their contribution. However, at very high levels, the probability increases that two events may pass through the gate. Manufacturers use a method of spectral stripping to correct for the false counts, but it is best to avoid the conditions that create the problem.

17.3.3.7 Test Source Vials

Glass test-source vials contain naturally occurring impurities such as potassium-40, thorium, and uranium. Their contribution appears at the lower energy portion of the spectrum. Plastic vials have a lower background, but they should be compatible with the liquid scintillation cocktail being used. Teflon vials are also available from most manufacturers.

17.3.3.8 Data Reduction for Liquid Scintillation Counting

Liquid scintillation counters normally provide minimal data reduction in their output. Basic data include the counting duration, count rate in one or more selected windows, and the date and time of counting initiation. A blank source (background) is normally counted with each counting batch and the output will provide the count rate of the blank to be subtracted from each test source.

The counting efficiency will also be provided by the output information. Its form of presentation in the output will depend on the calibration/counting (quench correction) method for determining

824 counter efficiency[4]. If the internal (standards addition) method is used the data generated by the
825 counter must be further manipulated in order to develop the counting efficiencies for each test
826 source. When using the external-standards method (quench curve), the scintillation spectrometer
827 will apply the quench corrected efficiency and give the test sample disintegration rate by applying
828 the corrected efficiency.

829 The radionuclide or gross concentration is provided by the following equation:

$$A_C = \frac{C_G - C_B}{\varepsilon_q V} \tag{17.21}$$

830 where:

831 C_G = the gross counting rate (source + background) (cps)
832 C_B = the counting rate of the blank (cps)
833 ε_q = the radionuclide quench corrected counting efficiency (c/d)
834 A_C = radionuclide or gross concentration (Bq/L or Bq/kg)
835 V = the volume or mass analyzed (L or kg)

836 17.4 Data Reduction on Non-Spectrometry Systems

837 Proportional counters are primarily used for counting of test sources for alpha and beta emitters.
838 Proportional counters may have entry windows for allowance of the emitted radiation into the
839 active portion of the detector or they may be windowless. These instruments are described in
840 Chapter 15. They are used for the determination of specific radionuclides, following chemical
841 separation to isolate the radionuclide, and for nonspecific (gross) analyses (Chapter 16). Counters
842 are equipped to count alpha and beta simultaneously in a given source and report the activity of
843 both.

844 The basic information obtained from a determination in a proportional counter is the number of
845 counts recorded in the detector within the allotted counting duration. However, modern
846 proportional counters take the data reduction process to the point of finality, i.e., producing the
847 test-source concentration and associated counting uncertainty, providing automatic instrument
848 background subtraction, and correcting for source self-absorption and alpha/beta crosstalk.

[4] For a discussion of liquid scintillation efficiency determination, see MARLAP Chapter 16, Section 16.5.2.1.

849 The instruments may also have protocols for developing the correction factors for self-absorption
850 and for crosstalk. In addition, they should have the capacity to track and evaluate the periodic
851 quality control checks (check source and background) performed on the instrument.

852 The basic equation used to calculate test-source concentrations is:

$$A = \frac{C_G - C_B}{\varepsilon} \tag{17.22}$$

853 where:
854 A = the activity of the radionuclide or gross activity (Bq)
855 C_G = the gross counting rate (source + background) (cps)
856 C_B = the instrument background counting rate (cps)
857 ε = the gross or radionuclide counting efficiency (c/d)

858 And the radionuclide or gross concentration is provided by the following equation:

$$A_C = \frac{C_G - C_B}{\varepsilon V} \tag{17.23}$$

859 where:
860 A_C = radionuclide or gross concentration (Bq/L or Bq/kg)
861 V = the volume or mass analyzed (L or kg)

862 The associated combined standard uncertainty is given by:

$$u_c(A_C) = \sqrt{\frac{u^2(C_G) + u^2(C_B)}{\varepsilon^2 V^2} + A_C^2\left(\frac{u^2(\varepsilon)}{\varepsilon^2} + \frac{u^2(V)}{V^2}\right)} \tag{17.24}$$

863 The above simple equations apply to counting either pure alpha or beta emitters and when no
864 correction for self-absorption is necessary (weightless sources). Modifications should be made in
865 the activity and concentration calculations when both alpha and beta particles are emitted by the
866 source, and when absorption and scattering within the source cause a reduction in the effective
867 efficiency.

Self-absorption factors are applied for sources where the internal attenuation of the alpha or beta particle is sufficient to affect the overall efficiency (Chapter 16). Commercially available proportional counters have a protocol for developing the self-absorption correction factors. These protocols process the data generated by counting a series of alpha calibration sources and a series of beta calibration sources, which both have varying masses of material, from "zero" to the maximum to be encountered in test sources (Chapter 16). The instrument is programmed to then fit the data to a mathematical function so the counting efficiency correction factor can be applied at any test-source mass within the range covered by the calibration source masses. A cubic polynomial is one option used for both alpha and beta counting efficiencies. A cubic polynomial has the form

$$\varepsilon_m = a_0 + a_1 m + a_2 m^2 + a_3 m^3 \qquad (17.25)$$

where:

m = is the residual mass of the test source
ε_m = the counting efficiency at mass m
a_i = constants determined by the data fit

The combined standard uncertainty of ε_m is given by

$$u_c(\varepsilon_m) = \sqrt{u^2(a_0) + \sum_{i=1}^{3} m^{2i} u^2(a_i) + 2\sum_{i=0}^{2}\sum_{j=i+1}^{3} m^{i+j} u(a_i, a_j) + (a_1 + 2a_2 m + 3a_3 m^2)^2 u^2(m)} \qquad (17.26)$$

When the identities of the alpha or beta emitting radionuclides are unknown, an additional component of uncertainty is needed to account for the dependence of the counting efficiency (and self-absorption) on the unknown particle energy.

Another option that is often used for the beta counting efficiency is an exponential curve, which has the form

$$\varepsilon_m = \varepsilon_{zero} e^{-am} \qquad (17.27)$$

where:

m = is the residual mass of the test source
ε_m = the counting efficiency at mass m
ε_{zero} = the "zero" mass counting efficiency
a = constant determined by the data fit

Then the combined standard uncertainty of ε_m is:

$$u_c(\varepsilon_m) = e^{-am}\sqrt{a^2u^2(m) + u^2(\varepsilon_{zero}) + m^2u^2(a) - 2m\,u(\varepsilon_{zero}, a)} \quad (17.28)$$

Again, an additional uncertainty component may be needed when the identity of the beta-emitting radionuclide is unknown.

Crosstalk, sometimes called "spill over," refers to the misclassification of alpha- and beta-produced counts in a proportional counter which is designed to count both particles simultaneously. It occurs when counts produced by alpha interactions in the detector are registered as beta counts and vice versa. In order to accurately record the alpha and beta activities of sources containing radionuclides emitting both particles, corrections must should be made for crosstalk.

The number of alpha interactions registered as beta counts will increase as the source self-absorption increases. The opposite is true for beta crosstalk, in that the number of beta interactions falsely designated as alpha counts decreases with source self-absorption. Thus, crosstalk correction factors vary with test-source mass and should be developed for the range of test-source masses to be encountered. Commercially available proportional counters have established programs to assist in the establishment of alpha and beta crosstalk factors. The algorithms to correct for crosstalk are presented below.

The alpha in beta crosstalk, X_α, is defined as:

$$X_\alpha = \frac{\beta}{\alpha + \beta} \quad (17.29)$$

The respective counts in the alpha channel (α) and those in the beta channel (β) counts are measured with a pure alpha-emitting source. Likewise, the beta in alpha crosstalk, X_β, is:

$$X_\beta = \frac{\alpha}{\alpha + \beta} \quad (17.30)$$

The respective alpha (α) and beta (β) count rates are measured with a pure beta-emitting source.

The relationship between X_α and X_β is given by:

$$\alpha = \alpha_d - \alpha_d X_\alpha + \beta_d X_\beta \quad (17.31)$$

$$\beta = \beta_d - \beta_d X_\beta + \alpha_d X_\alpha \tag{17.32}$$

Equation 17.31 states that the recorded alpha count rate, α, consists of the actual alpha count rate, α_d, (the total alpha count rate in both the alpha and beta channels due to only alpha interactions), minus those alpha interactions recorded in the beta channel, plus those beta counts recorded in the alpha channel. Equation 17.32 states the equivalent of Equation 17.31 for beta counts. Solving the equations simultaneously for α_d and β_d gives:

$$\alpha_d = \frac{\alpha - X_\beta(\alpha + \beta)}{1 - X_\alpha - X_\beta} \tag{17.33}$$

$$\beta_d = \frac{\beta - X_\alpha(\alpha + \beta)}{1 - X_\alpha - X_\beta} \tag{17.34}$$

Their associated combined standard uncertainties are:

$$u_c(\alpha_d) = \frac{\sqrt{u^2(X_\alpha)\alpha_d^2 + u^2(X_\beta)(\alpha_d - \alpha - \beta)^2 + u^2(\alpha)(1. - X_\beta)^2 + u^2(\beta)X_\beta^2}}{1 - X_\alpha - X_\beta} \tag{17.35}$$

$$u_c(\beta_d) = \frac{\sqrt{u^2(X_\beta)\beta_d^2 + u^2(X_\alpha)(\beta_d - \alpha - \beta)^2 + u^2(\beta)(1 - X_\alpha)^2 + u^2(\alpha)X_\alpha^2}}{1 - X_\alpha - X_\beta} \tag{17.36}$$

Since crosstalk factors vary with radionuclide, additional uncertainty components may be needed when the identities of the alpha and beta emitting radionuclides are unknown.

Processors execute many other functions for instruments which do not perform spectrometry. These instruments include proportional counters, scintillation detectors, ionization chambers, and special instruments (Chapter 15). The functions performed by processors may include instrument control (sample change, gas flow control, etc.) and the calculations necessary to convert the basic counting information to final form data or to some intermediate step.

Data reduction functions which may be performed for scintillation detectors, ionization chambers, and special instruments include the following:

- Background determination and subtraction;
- Conversion of total counts to counts per second;
- Calculate activity using calibration data;
- Calculate concentration using activity and operator input data;
- Perform efficiency calibrations;
- Calculate counting and total uncertainty;
- Cross talk determination and correction;
- Self-absorption corrections;
- Radioactive decay corrections; and
- Quality control (QC) functions (efficiency and background verification).

The output of manual systems usually requires further reduction to render it usable. The information generated by processor-based systems may also need further processing.

These additional calculations may be performed using a calculator or by a computer using general or custom software programs. The data may be electronically transferred to the processing computer by a local area network (LAN) or on a computer disk. In some cases the processing software may be part of the LIMS.

17.5 Reporting Data

Quality assurance planning documents will give the level of data reporting required. This level will vary from simply confirming the presence or absence of an analyte to a complete reporting of all measurements, calibration data, documentation of the performance of laboratory processes, provision of certain instrument counting reports, and QC sample results and analysis. Another way of viewing this is as a tiered approach where preliminary studies or site surveys may only require a minimum of data reporting, while a final site survey may require a detailed reporting of the results. The necessary elements for data reporting are connected to the purpose for which the data will be used (data quality objectives).

MARLAP recommendations for data reporting are that the reported value of a measurement result: (1) be reported directly as obtained, with appropriate units, even if they are negative values, (2) be expressed in an appropriate number of significant figures, and (3) include an unambiguous statement of the uncertainty. The appropriate number of significant figures is determined by the magnitude of uncertainty in the reported value. Each reported measurement

result should include the value and an estimate of the uncertainty (expanded uncertainty) (ANSI 42.23).

17.5.1 Sample and Analysis Method Identification

Sample data are normally reported by sample number, including both the field (project) and laboratory assigned identifiers. In addition, the submitting laboratory should be identified as well as the analysis method (ANSI 42.23, p. 38). Other information which can assist in the review and interpretation of the data may be requested. This could include sample collection date (decay correction reference date), analysis date, chain-of-custody (COC) number, and site or project name.

17.5.2 Units and Radionuclide Identification

The individual radionuclides should be identified or, for gross analyses, the category, e.g., gross alpha/beta, should be reported. Reporting units are likely specified by project planning documents. If not specified, when possible, International System of Units (SI) units are preferred. However, since regulatory compliance levels are usually quoted in traditional radiation units, it may be appropriate to report in both SI and traditional units with one being placed within a parenthesis. Both the SI and non-SI units are shown in Table 17.1 for common matrices.

TABLE — 17.1 Units For Data Reporting

Matrix	In Non-SI Units	In SI Units	Conversion Factor From Non-SI to SI Units
Airborne Particulates and Gas	pCi m^{-3}	Bq m^{-3}	3.70×10^{-2}
Liquids	pCi L^{-1}	Bq L^{-1}	3.70×10^{-2}
Solids	pCi kg^{-1} or pCi g^{-1}	Bq kg^{-1}	3.70×10^{-2} or 37
Surfaces	dpm / 100 cm^2	Bq / 100 cm^2	1.67×10^{-2}

17.5.3 Values, Uncertainty, and Significant Figures

The value, as measured, including zero and negative numbers, and the measurement uncertainty (either expanded uncertainty or the combined standard uncertainty) should be reported in the same units (Chapter 19). In general, environmental radiation measurements seldom warrant more than two or three significant figures for the reported value, and one or two significant figures for the uncertainty. As recommended in Chapter 19, Section 19.3.6, the measurement uncertainty should be rounded to two significant figures, and both the value and uncertainty reported to the

resulting number of decimal places. For example, a value of 0.8961 pCi/L with an associated measurement uncertainty of 0.0234 should be reported as 0.896 ± 0.023 pCi/L. The MDC should be reported to two significant figures (ANSI 42.23, p38). It should be noted that truncation should only occur in reporting the final results (Section 18.3.6).

17.5.4 Other Information to be Provided on Request

Information which should be documented and retained for provision, if requested, includes (ANSI 42.23, p38):

- Total weight or volume of the sample submitted and analyzed;
- Identification and documentation of specific analysis processes and analyst;
- Specific analytical parameters, i.e., chemical yields, counting times, decay factors, efficiency of detectors used;
- Date, time, and place of sampling;
- Sample receipt information; and
- QC data demonstrating the quality of the measurement.

17.6 Data Packages

Project planning documents (Chapter 4) and analytical statements of work (Chapter 5) will usually define the requirements of the final data submittal. Many projects will specify a data package which contains not only the data reports described in the preceding section, but other supporting information to further describe, document, and define the analytical process. These additional requirements may be instituted to provide a basis for data verification/validation (Chapter 8), the purpose of which is to confirm that the data meet project quality objectives (Chapter 2). Material which may be required as part of a data package is discussed in Chapter 5.

17.7 Electronic Data Deliverables

Many project planning documents and SOWs require that laboratory data be delivered in electronic format, commonly called electronic data deliverables (EDD). This allows the data to be directly entered into a project database or, in some cases, into validation programs, and avoids

transcription errors. There is no universal format for presenting EDDs, so the laboratory may be required to produce them in various formats. While the record structure of the EDD may vary in terms of the length and order of the fields, it is likely that the following are examples that may be requested:

- Field Sample Number
- Laboratory Sample Number
- Sample Collection or Reference Date
- Sample Receipt Date
- Analysis Date
- Result Identifier (sample or type of QC sample)
- Radionuclide
- Result
- Results Units
- Measurement Uncertainty
- Sample Aliquant Size
- Aliquant Size Units
- Minimum Detectable Concentration
- Minimum Quantifiable Concentration (MQC)

More information on EDDs may be found at the following websites:

More information on EDDs may be found at the websites listed here. The U.S. Department of Energy EDD may be found at: (http://www.em.doe.gov/namp/pitimp.html) or (http://www.em.doe.gov/namp/deemmeet.html). Another EDD that is more general has been developed. It is called the General Electronic Data Deliverable (GEDD) and may be found at the website: (http://ersmo.inel.gov/edd/gedd.html#Entity Relationship Diagram). The EPA Environmental Data Registry may be found at: (http://www.epa.gov/edr/). U.S. Air Force Environmental Resources Program Management System (ERPRIMS) website: (http://www.afcee.brooks.af.mil/ms/msc_irp.htm) also provides useful information on environmental databases and EDDs.

EDDs may be transmitted by direct electronic transfer, e-mail, or by diskette.

17.8 References

17.8.1 Cited References

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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 requests are more stringent than typical laboratory QC needs, the project manager and the laboratory should confer to see whether the laboratory can accommodate the tightened QC requirements. Laboratory data should be produced in a quality system[1] that incorporates planning, implementing, and internal assessment of the work performed by the laboratory, including QC. While this chapter focuses on laboratory 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. General requirements for testing laboratories can be found in ISO/IEC 17025.

The 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.

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

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[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).

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.

Table 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.

TABLE 18.1 — Problems leading to loss of analytical control

Radiochemical Processing	Source Preparation	Instrument Related	Other
Laboratory blunder	Laboratory blunder	Laboratory blunder	Laboratory blunder
Processing difficulty	Poor mounting	Electronic malfunction • preamplifier • power supply • guard	Data transcription error
	Poor plating		

Radiochemical Processing	Source Preparation	Instrument Related	Other
Questionable reagent purity	Improper geometry	• analog to digital convertor (ADC) • gain • high voltage	Incorrect units Calculation error
Low tracer/carrier recovery	Incorrect thin plastic film thickness	• discriminator • pole zero • shape constant	Software limitation
Excessive tracer/carrier recovery	Improper plating on the planchet	Improper source or sample geometry Poor counting statistics	Computer problem Loss of electrical power
Inaccurate aliquanting of tracer/carrier	Excessive source mass	Poor detector resolution Detector contamination	Electrical power fluctuations
Sample aliquanting inaccuracy	Uncorrected self absorption	Inappropriate/out-of-date efficiency, background or calibration factor	Mislabeling
Cross-contamination	Quenching Recoil contamination	Background shift	Loss of sample
Inadequate dissolution of sample		Incorrect nuclear transformation data or other constants Variable memory effects	Insufficient sample information
Complex matrix		Peak/calibration shift	Data processing problem
Sample heterogenity		Counting gas • pressure too high, too low, or variable • gas impurity Loss of vacuum/coolant Temperature and humidity fluctuation Measurement problem	Interfering radionuclides

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.

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 Appendix C). 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 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 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, 6th Edition, 1990.

Figure 18.1 illustrates a typical control chart using counting data of a standard 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 like that shown on the left of the vertical axis in the figure. 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 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.

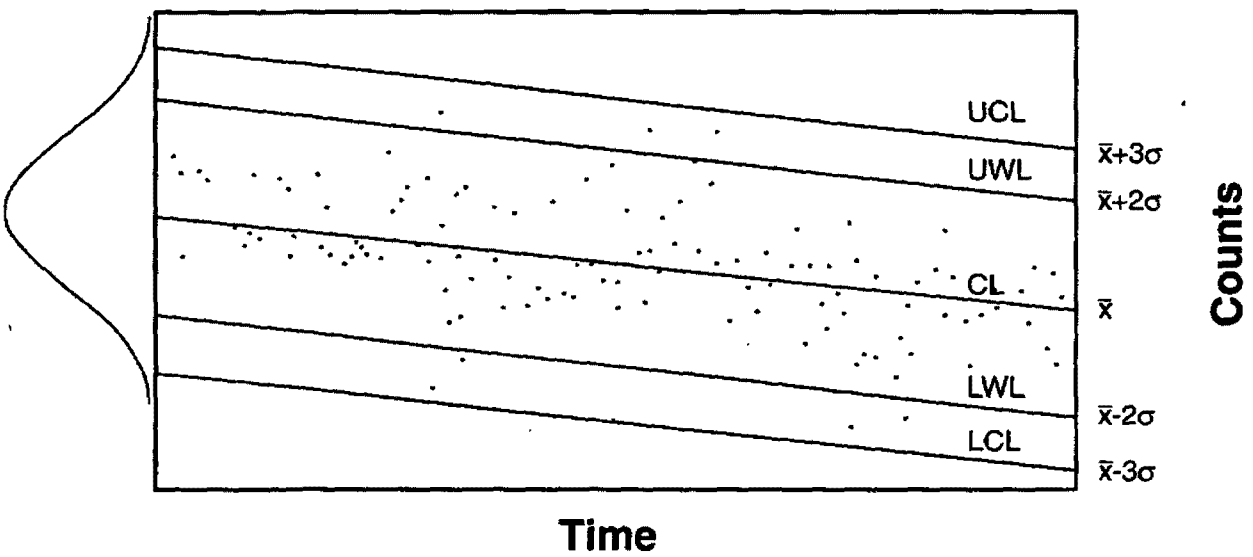

FIGURE 18.1 — Control chart for daily counting of a standard reference source, with limits corrected for decay. Statistical nature of chart is illustrated on the left by the Gaussian curve.

18.3.3 Measurement Uncertainty

Issue: Since laboratory radioactivity measurements always involve uncertainty, 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 observe individual *Z* score values 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 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 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 are 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. When reagent blank results are used to correct sample activities, it is important that the blank results be carefully monitored using control charts.

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

$$Z_{\text{Blank}} = \frac{x}{u_c(x)} \qquad (1)$$

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 18.2 and described below.

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. Laboratory cleaning practices and new or recently restocked reagents

should be checked. When a sudden, significant increase in the blank occurs in conjunction with the introduction of new reagents through restocking or other changes, the causes should be investigated and if the reagent is contaminated, the reagent contributing the activity should be discarded and replaced. Particular attention should be paid to the samples counted directly prior to the contaminated blank, since small amounts of residues from these samples can contaminate the detector 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.

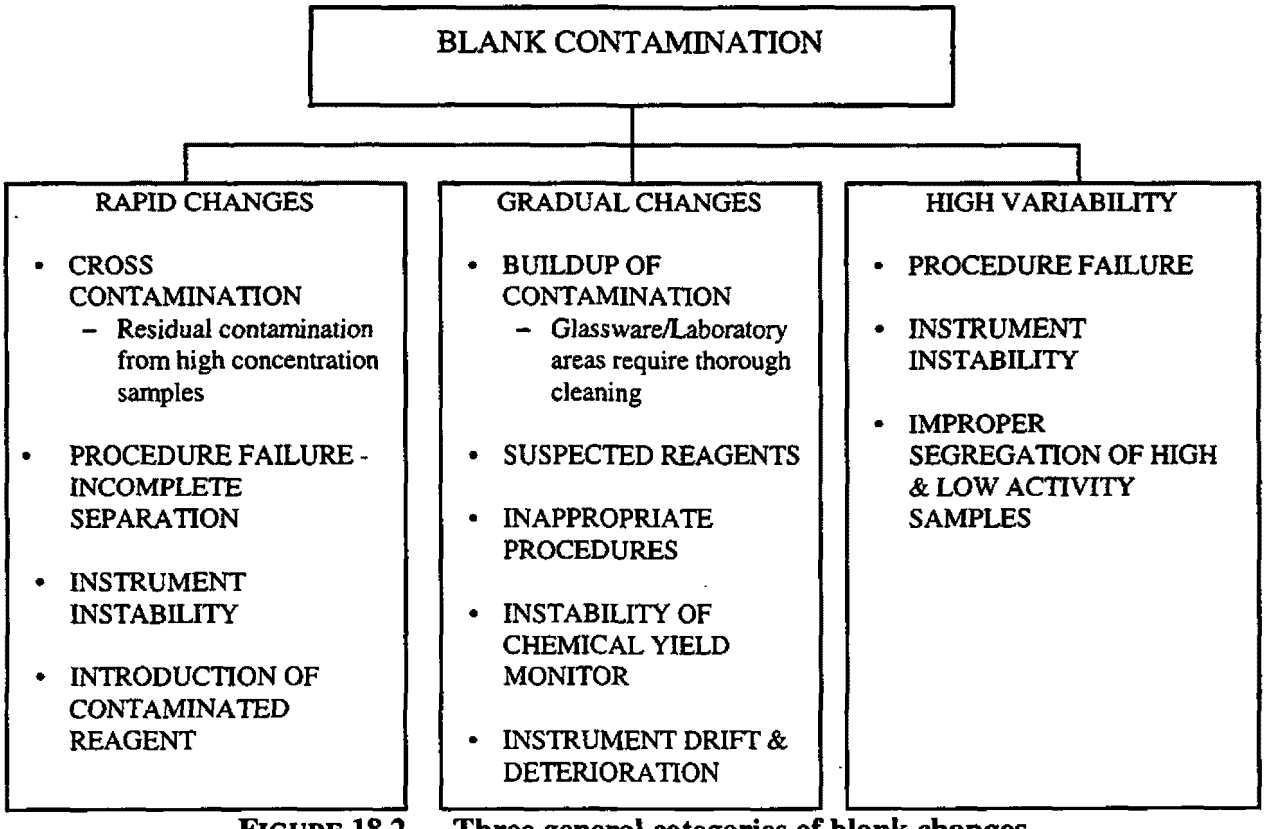

FIGURE 18.2 — Three general categories of blank changes

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 radiometric determinations near these levels. Large variations in blank values typically indicate problems related to instruments or sample processing, 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 precision of the measurement process. 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 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 homogeneous. This facilitates dividing the samples into equivalents fractions or aliquants. 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 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 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

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

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 18.3) 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.

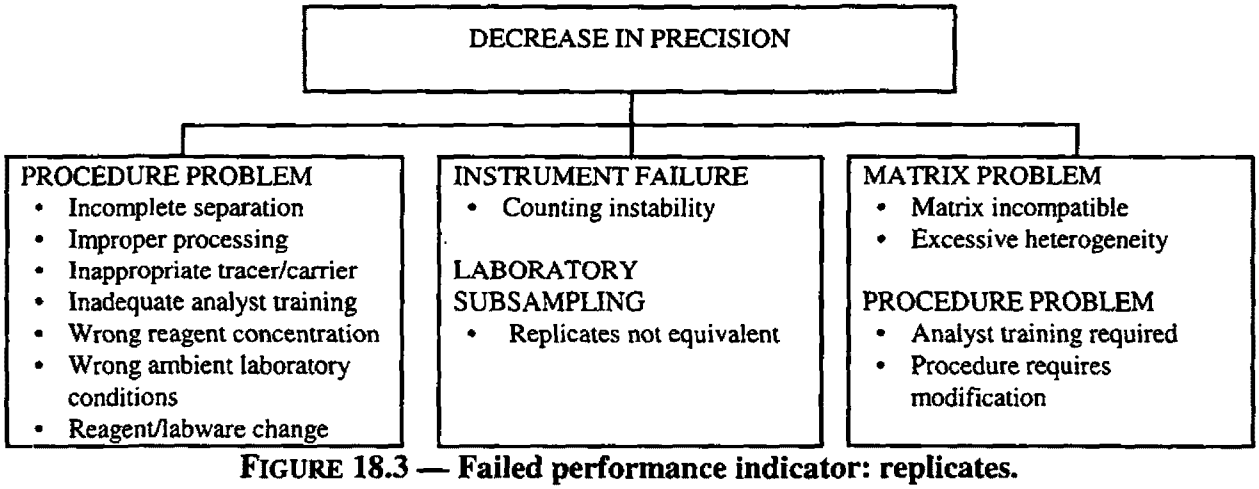

FIGURE 18.3 — Failed performance indicator: replicates.

- Matrix – Sample constituents interfere with preparation chemistry, e.g., coprecipitation of interfering non-analyte 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 (MS) is an aliquant of a sample prepared by adding a known quantity of target analytes to a specified amount of sample and subjected to the entire analytical procedure to establish if the method or procedure is appropriate for the analysis of the particular matrix. A matrix spike duplicate (MSD) is a second replicate matrix spike prepared in the laboratory and analyzed to evaluate the precision of the measurement process.

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 that spikes are prepared 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 bias. Tracking sets of LCS and matrix spike results can give laboratory personnel an indication of the magnitude of 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, aqueous samples tends to be less affected than other media like soils or heterogeneous materials. However, multi-phase fluids, high solid content, 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 methods performance on clean or slightly contaminated samples. Conversely, matrix spikes and LCSs may be spiked at high levels for groups of highly contaminated samples. The laboratory should try to spike at or near the action level or level of interest for the project.

Possible numerical performance indicators for laboratory control samples and matrix spikes are

$$Z_{LCS} = \frac{x - d}{\sqrt{u_c^2(x) + u_c^2(d)}} \tag{3}$$

$$Z_{MS} = \frac{x - x_0 - d}{\sqrt{u_c^2(x) + u_c^2(x_0) + u_c^2(d)}} \tag{4}$$

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.

Elevated or depressed results for site-specific MSs need to be interpreted 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 determined 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 national scale of measurements 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. The 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

$$Z_{CRM} = \frac{x - d}{\sqrt{u_c^2(x) + u_c^2(d)}} \quad (5)$$

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 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 18.2a), while the four "man-made" radionuclides tended to have Weibull distributions (Table 18.2b). There are also 11 other radionuclides where the activity concentrations are not certified at this time but may be at some future time (Table 18.2c).

TABLE 18.2a — Certified Massic activities for natural radionuclides with a normal distribution of measurement results

Radionuclide	Mean ± $2s_m$ ($mBqg^{-1}$)	Tolerance Limit (2.5 to 97.5%) ($mBqg^{-1}$)	Number of Assays	Half-Life ± 1s (In years)
^{40}K	225 ± 5	190 – 259	31	$(1.277 \pm 0.008) \times 10^9$
^{226}Ra	12.7 ± 0.4	10.3 – 15.0	21	1600 ± 7
^{228}Ra	13.3 ± 0.8	9.2 – 17.4	20	5.75 ± 0.03
^{228}Th	12.1 ± 0.3	9.7 – 14.6	40	1.9131 ± 0.0009
^{230}Th	12.0 ± 0.5	9.6 – 14.4	18	75380 ± 300
^{232}Th	13.0 ± 0.3	11.6 – 14.3	18	$(1.405 \pm 0.006) \times 10^{10}$

Table 18.2b — Certified Massic activities for anthropogenic radionuclides with a Weibull distribution of measurement results

Radionuclide	Mean ± $2s_m$ ($mBqg^{-1}$)	Tolerance Limit (2.5 to 97.5%) ($mBqg^{-1}$)	Number of Assays	Half-Life ± 1s (In years)
^{90}Sr	4.4 ± 0.3	2.1 – 8.4	49	28.87 ± 0.04
^{137}Cs	12.7 ± 0.2	10.8 – 15.9	76	30.07 ± 0.03
^{238}Pu	2.29 ± 0.05	1.96 – 2.98	65	87.7 ± 0.3
^{239}Pu + ^{240}Pu	10.4 ± 0.2	9.3 – 13.2	84	24110 ± 30 6564 ± 11

Table 18.2c — 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 ($mBq\ g^{-1}$)	Range of Reported Results ($mBq\ g^{-1}$)	Number of Assays	Half-Life ± 1s (In years unless listed as minutes, hours, or days)
^{129}I	0.009	0.006 – 0.012	6	$(1.57 \pm 0.04) \times 10^7$
^{155}Eu	1.4	1.2 – 1.5	2	4.68 ± 0.05
^{210}Po	14	12 – 15	5	138.376 ± 0.002 d
^{210}Pb	24	14 – 35	19	22.3 ± 0.2
^{212}Pb	14	13 – 14	5	10.64 ± 0.01 h
^{214}Bi	15	9 – 20	5	19.9 ± 0.4 m

Radionuclide	Mean (mBq g^{-1})	Range of Reported Results (mBq g^{-1})	Number of Assays	Half-Life ± 1s (In years unless listed as minutes, hours, or days)
^{234}U	12	9 – 15	68	$(2.45 \pm 0.02) \times 10^5$
^{235}U	0.6	0.1 – 1.4	63	$(7.038 \pm 0.006) \times 10^8$
^{237}Np	0.007	0.004 – 0.009	9	$(2.14 \pm 0.01) \times 10^6$
^{238}U	12	7 – 16	76	$(4.468 \pm 0.003) \times 10^9$
^{241}Am	10	7 – 18	97	432.7 ± 0.6

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

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 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}U, 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 recovery for each sample analysis, e.g., *Procedure 908.1 for Total Uranium in Drinking Water* (EPA, 1980b). In such cases, chemical recovery is typically addressed by analyzing a group of prepared standards by the same protocol and the results are analyzed statistically to derive a chemical recovery 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 recovery, 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 18.4 and discussed below.

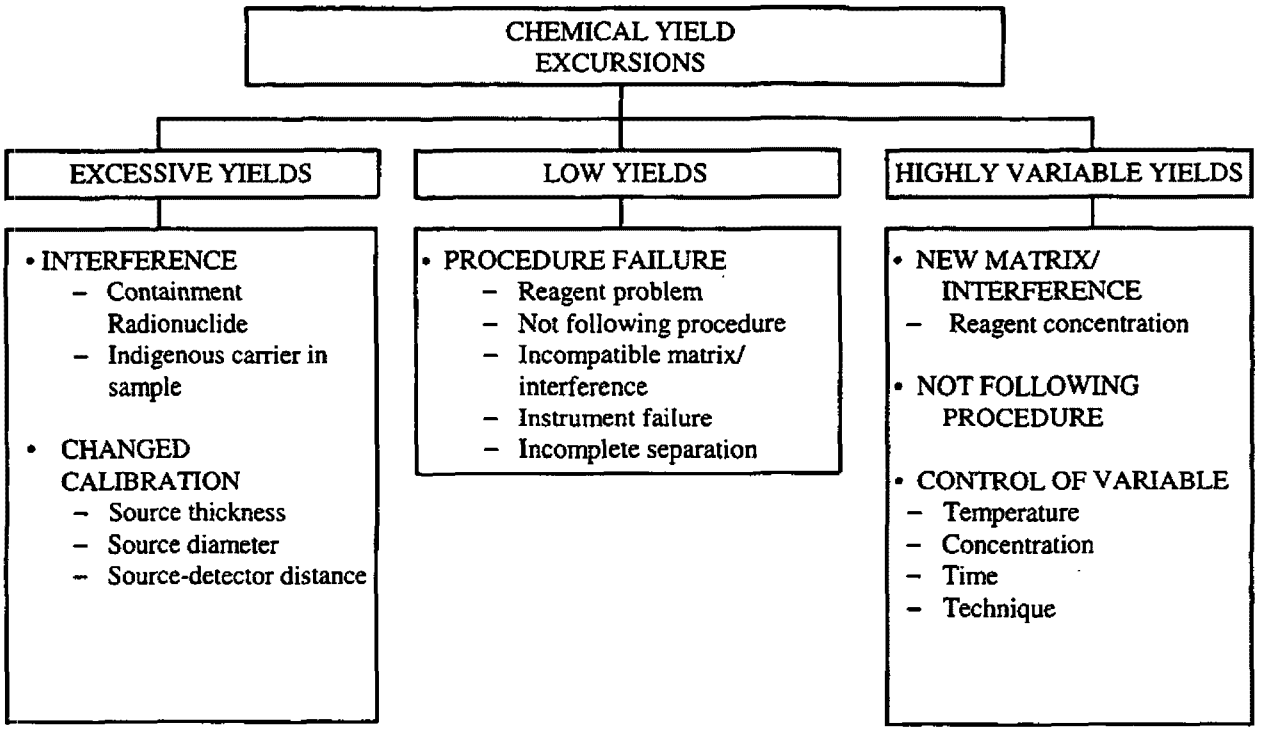

FIGURE 18.4 — Failed performance indicator: chemical yield

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 Chapters 15 and 16 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 the laboratory Quality Manual.

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). For discussions on possible contamination, refer to Section 18.4.1. 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 to instrument background produce a fairly constant count rate, given sufficient measurement time (i.e., dark current, cosmic radiation, construction material impurities). 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 the laboratory's Quality Manual, as appropriate. 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 (2000) *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 observation 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 18.3 presents reasons for changing backgrounds.

TABLE 18.3 — Instrument background evaluation

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

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 based on 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 sample, 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 sample can be absorbed by the sample itself (self

[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.

absorption), as well as other materials placed between the source and the detector, i.e., sample container, detector housing and shielding (NCRP 58).

- Backscatter – Radiation emitted by the sample can hit the sample container 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 disintegration rate of the source being assayed. This relationship is called the efficiency calibration—typically expressed in counts per second/ disintegration 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 kilo electron volts (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 sample is often helpful in eliminating sample geometry as a source 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 sample 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 sample 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 samples that have been improperly prepared for counting can result in contamination of or physical damage to the detector, it is strongly recommended that every sample 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 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 with efficiency related to the quality or flow of counting gas.

- Anti-coincidence systems with guard detectors – Electrical problems with the anti-coincidence circuits that 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 is provided in Chapter 16. 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 (e.g., ^{137}Cs or ^{60}Co) 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 Table 18.5.

- HPGe and Ge(Li) Photon Detectors. Energy calibrations are typically verified using a check source on a day of use basis. Every sample 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 or 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. This variation is accounted for by the Fano factor. Because several poorly understood factors degrade resolution in a semiconductor detector, an empirical value of the Fano factor should be used.

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 sample 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 is typically 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 to the most probable peak height. The sources of fluctuations that contribute to the standard deviation are dependent on the type of detector.

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. Control 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 because the FWHM is inversely proportional to the energy. 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.

Proportional counters are not used as spectrometers in many laboratories, so it is not necessary to perform checks for resolution and peak shape.

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.

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 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. Table 18.4 lists common problems, the implied root cause of the problem, and possible corrective actions.

TABLE 18.4 — Root cause analysis of performance check results

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 Detector problem
FWTM: FWHM changed	Electronics problem	Ensure high voltage is set properly Detector problem

Observed Problem	Implied Root Cause	Possible Corrective Actions
	Source problem	Repeat sample preparation and recount Reanalyze sample Check with weightless (plated) source
No peak or broad peaks	Electronics problem	Ensure that high voltage is correct Detector problem
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 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 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 samples 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 or verified. The operating potential is usually selected in the middle of the plateau. It remains advisable to assure that the operating point is as far as practical above the plateau knees, and in any case not less than 50 to 100 volts. 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 potential variance. 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 potential 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 sample 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 standards 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 sample's efficiency as a function of sample weight. The diameter and the composition of the sample planchette, not just the weight, should be identical with what was used for routine samples. This allows calculation of the corrected amount of activity regardless of the sample 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 electroplated sources, crosstalk may be as low 1 percent for betas in the alpha channel and 3 percent for alphas in the beta channel. 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_{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_{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 sample increases, the alpha into beta crosstalk increases, due to the degradation of the alpha particle energy by interaction with sample 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, test samples 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, 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: A liquid scintillation counter is essentially a spectrometer that utilizes a multi channel analyzer to differentiate alpha or beta emission energies. These samples are subject to interferences from a variety of sources for which corrections should be made to produce useful data. A detailed discussion of liquid scintillation counting is provided in Chapter 15.

18.5.6 Summary

Table 18.5 provides some example calibration needs, performance frequency, and performance criteria, listed by detector type. Individual laboratories may be more or less stringent. These items are just presented as examples for consideration in this section. The table is presented mainly for the reader to establish their own criteria and is not intended to be a set of minimum requirements. For additional sources of information, see the calibration frequencies for several detector systems given in ASTM E181 and ANSI N42.12.

TABLE 18.5 — Instrument calibration: example frequency and performance criteria

Example Calibration Needs	Measurement Parameters	Performance Frequency	Performance Criteria
Gas Proportional System			
Initial calibration	Plateau checks as applicable	After repairs or major maintenance on control of system is re-established	Plot voltage versus counting activity to estimate proper operating voltages for both alpha and beta
	Crosstalk or sensitivity as applicable	After repairs or major maintenance on control of system is re-established	Crosstalk of alpha in beta: less than 10%; Crosstalk or sensitivity of beta in alphas: less than 1%
	Counting efficiency to calculate activity in sample	Upon incorporation of new or changes protocols	Counting uncertainty <1%; <3% uncertainty (2s) over calibration range
	Weight of solids, when mass loading is applicable, to calculate sample activity		Establish a curve for efficiency versus mass loading; <3% uncertainty (2s) over calibration range
Background counting	Count detector background using contamination-free clean planchet	One per week or batch when the system is in use	Establish a background count rate value for total alpha and beta, with N>1000

Example Calibration Needs	Measurement Parameters	Performance Frequency	Performance Criteria
Counter control or control standard	Use a source of appropriate energies	One per day when the system is in use	Control limits: three sigma or ± 3%, whichever is greater
Gamma Spectrometry			
Initial calibration	Detector energy calibration	After repairs or major maintenance if control of system cannot be re-established	Covers energy range of desired nuclides; resolution should be sufficient to separate gamma-ray lines of interest from background peaks and other interfering lines
	Counting efficiency matrix- and geometry-specific		Span energy range of nuclide of interest
Background	Counter detector background to establish background level	Minimum of every week or after analytical run, whichever is longer	
Counter control or control standard	Multi energy source covering the general energy calibration range	One per week or after analytical run, whichever is longer	Control limits: three sigma or ± 3%, whichever is greater
Alpha Spectrometry			
Initial calibration	Energy calibration	After repairs or major maintenance if control of system cannot be re-established	No specific criteria, pending on total channel and range of energy spectrum of desired nuclides
	Counting efficiency matrix- and geometry-specific		Span energy range of nuclide of interest
Background	Counter detector background to establish background level	Minimum of every other week or after analytical run, whichever is longer	
Counter control or control standard	At least two isotopes Monitor peak location, resolution and efficiency (where counting efficiency is an analytical requirement).	One per week or after analytical run, whichever is longer	Control limits: three sigma or ± 3%, whichever is greater
Liquid Scintillation			
Initial Calibration	Dark blank to check photomultiplier tube	After mechanical or electronic repairs	Check against manufacturer's specifications
Calibration	External (instrumental) calibration	After repairs or major maintenance if control of system cannot be re-established	Check against manufacturer's specifications

Example Calibration Needs	Measurement Parameters	Performance Frequency	Performance Criteria
Method Calibration (Determining quenching)	Quench curve (at least five points)	If matrix or cocktail changes	
	Internal standard	Add to each sample type	
Background	Counter detector background	One per day or analytical batch when the system is in use	
Counter control or control standard		One per day or batch when system is in use	Control limits: three sigma or ± 3%, whichever is greater
Batch-approach calibration (Alternative approach)	Minimum two matrix-matched standards and blanks	One per batch	Counting efficiency control limits: three sigma or ± 5%, whichever is greater

Sources: ASTM E181; ANSI N42.12.

18.5.7 Non-Nuclear Instrumentation

Radioactivity and radionuclide measurement techniques also employ the use of non-nuclear instrumentation such as mass spectrometry, fluorimetry, phosphorimetry, and fission tract. Although these instruments are not covered in MARLAP, 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 secular 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 19). 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 19). The MDC is defined as the smallest concentration of an analyte that has a specified probability of detection, typically 95 percent. 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 Secular Equilibrium

Issue: It is sometimes necessary to ensure that target radionuclides are in secular 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.

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 disintegration which 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}Ra, 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}Ra 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 calculational 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 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 (General Electric, 1984). 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. Typical ^{235}U enrichments range from 2 percent for 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.[4] 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 ^{234}U are alpha emitters with considerably different physical half-lives and specific activity, 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

[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.

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. Consecutive counting of the sample may confirm the radionuclide impurity by analyzing the decay rate between counting events.

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 time of collection in the field. 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 period over which their direct progeny are allowed to come to secular equilibrium; this is followed by chemical separation, purification and counting of the progeny. After counting, the degree of the progeny's ingrowth is calculated, based on the radionuclides' half-lives and the elapsed time between separation and counting. 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 (http://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.

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 there is an additional correction factor in the algorithms for these samples (decay factor), they are more susceptible to measurement uncertainty than longer-lived radionuclides.

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 or other physical aspects 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 concentration at which this procedure cannot overcome the interferences and should not be used.

Samples that contain natural concentrations of stable or unstable compounds that an analytical procedure adds to the sample for a specific purpose (carrier or tracer) may also be problematic because the sample's concentration interferes with the analysis. Because barium is used as a carrier, water samples that contain 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 unstable 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. Samples assayed for ^{228}Ra may contain measurable amounts of ^{90}Sr that require corrections based on differences in half-life (^{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 recovery. 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. look for ^{238}U peak in a Pu spectra. If the ^{238}U peak is present, ^{234}U might be an interference in the ^{239}Pu and ^{240}Pu determinations. Data can be corrected or the sample may require reanalysis.

Each analytical method should be evaluated with respect to interferences, when its use is proposed or at least prior to their implementation in the laboratory. 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 recovery 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 inherent concentrations of carrier/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 hydroscopic, and continue to gain weight following preparation in planchettes as they absorb moisture from the air. These changes could be detected by reweighing the planchettes 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, predominantly ^{210}Po and ^{137}Cs, which have alpha and beta emissions, respectively. An alternative approach is to thoroughly dry each planchette, 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 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;
- 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 for specific analytes and matrices. Blind samples can be internal or external, and either single or double. External blind 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 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 them 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 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. In the case of replicates , the analyst is not aware that two samples are the same; for spiked samples, 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 the same as a single blind except that it is submitted for analysis as a routine sample. The sample should be identical in appearance to a routine sample, and the analyst is not forewarned of the analytes in the sample. 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. 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 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), and Multi-Analyte Performance Evaluation Program (DOE MAPEP).

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 PE programs should be addressed.

18.6.7 Calibration of Apparatus Used for Weight and Volume Measurements

Issue: Fundamental to all quantitative analysis is the use of the proper weights 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.

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 weights are used to perform the daily calibration check, depending on application. Over time, daily wear and tear on the weights can affect calibration, so it is a good idea to get them periodically re-certified or to purchase new weights.

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" requires the complete emptying of the vessel to yield the specified volume. "To deliver" glassware does not require complete emptying. Specified volumes for this type of apparatus 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.

The most important purpose for 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 variability 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 strict 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,

1754 although the X chart is often used with other types of distributions. (The data may be tested for
1755 normality using the procedure described in Attachment 19F.)

1756 In order to use Procedure 18.1, an unbiased estimate of the standard deviation of the measured
1757 values $X_1, X_2, \ldots, X_n$ is required. Although the experimental variance s^2 of the data is an unbiased
1758 estimate of the true variance σ^2, taking the square root of s^2 generates a bias . The experimental
1759 standard deviation s is given by the equation

1760

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

1761 If the data are (approximately) normally distributed, s should then be divided by the value of c_4
1762 shown in Table 18A-1 below for the number of degrees of freedom $\nu = n - 1$. Thus, σ is esti-
1763 mated by s / c_4. The factor c_4 is equal to
1764

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

1765 where Γ denotes the *gamma function* (NBS 1964), but it is well approximated by $c_4 \approx \frac{4n-4}{4n-3}$. For
1766 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

$$\frac{2\sigma}{\sqrt{\pi}} \approx 1.128\,\sigma \tag{3}$$

which may be estimated by

$$\overline{\mathrm{MR}} = \frac{1}{n-1}\sum_{i=1}^{n-1}\left|X_{i+1} - X_i\right| \tag{4}$$

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 $\tilde{\sigma}$ 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:

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

If n is less than 20, a higher rate of false warnings and failures may occur because of the increased uncertainties of the estimates $\bar{X}$ and $\bar{\sigma}$. 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 $\bar{X} = 22{,}168.3 / 20 = 1{,}108.415$

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

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

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

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

18A.3 $\bar{X}$ 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 $\bar{X}$ and the standard deviation $\bar{\sigma}$ 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

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

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 $\bar{X}$ and $\bar{\sigma}$. 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 $\bar{X} = 22{,}168.3 / 20 = 1{,}108.415$

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

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

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

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

18A.4 *R* Charts

The range of a set of values is the difference between the largest value and the smallest. Plotting ranges on a range chart or *R chart* is used to monitor within group variability because *R charts* detect changes in variability more easily. Duplicate measurements for any radiochemistry indicator are made and the difference between the duplicates are used to construct the central line (the mean range), and the control and warning limits in a similar fashion as in the *X chart*. Procedure 18.2 may be used to determine the parameters of the *R chart*.

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, $\bar{R}$, using the formula

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

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

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

The factor 3.267 is called "D_4" in references on statistical quality control. The value of D_4 is smaller when the range of a larger group is monitored. When the group size is at least seven, there is also a factor called D_3, which may be used to calculate a lower control limit for the range. 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.

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 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 Poisson 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, and obtaining 10,000 counts is therefore 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 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, preferably near 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 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

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

and the standard deviation by

$$s = \sqrt{CL}$$

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:

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

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 $N_1, N_2, \ldots, N_n$. (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, $\exp(-\lambda(\Delta t + 0.5t_i))$). 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

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

and the standard deviation s by

$$s = \sqrt{CL}$$

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

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

If $\sum t_i d_i < 20TD$, 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

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

and

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

Step 4 The control limits and warning limits are

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

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

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

3. Estimate the central line by

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

and the standard deviation s by

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

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

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

18A.6 References

American National Standard Institute (ANSI) N42.23. *Measurement and Associated Instrumentation Quality Assurance for Radioassay Laboratories.* 1996.

American Society for Testing and Materials (ASTM) D6299, *Standard Practice for Applying Statistical Quality Assurance Techniques to Evaluate Analytical Measurement System Performance,* 2000

American Society for Testing and Materials (ASTM) E882, Standard Guide for *Accountability and Quality Control in the Chemical Analysis Laboratory.*

American Society for Testing and Materials (ASTM) MNL 7, *Manual on Presentation of Data and Control Chart Analysis* ASTM Manual Series, 6th Edition, 1990.

National Bureau of Standards (NBS). 1964. *Handbook of Mathematical Functions.* M. Abramowitz and Stegun, I., Editors.

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

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

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 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. 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 $\sum_{i=1}^{n} N_i$ and $\sum_{i=1}^{n} w_i$.
3. Estimate the mean decay-corrected count rate by

$$\hat{r} = \frac{\sum_{i=1}^{n} N_i}{\sum_{i=1}^{n} w_i} \tag{2}$$

4. Calculate the chi-square statistic as follows:

$$\chi^2 = \frac{1}{\hat{r}} \sum_{i=1}^{n} \left(\frac{N_i}{w_i} - \hat{r} \right)^2 w_i \tag{3}$$

5. Determine the quantile $\chi^2_{1-\alpha}(n - 1)$ (see Table G.1 in Appendix G). Reject the null

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[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 $\hat{r} = \sum N_i / \sum t_i d_i$. So, the sum $\sum (N_i / t_i d_i - \hat{r})^2 / (r / t_i d_i)$ is approximately chi-square with $n - 1$ degrees of freedom. 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 $\sum (N_i - \bar{N})^2 / \bar{N}$, 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 $t_i \propto w_i$.

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.

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.1, 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

$$\xi_D^2 = \frac{1}{\mu}\left(\frac{\chi^2_{1-\alpha}(n-1)}{\chi^2_{\beta}(n-1)} - 1\right) \tag{4}$$

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

$$\xi_D^2 = \frac{1}{10{,}816}\left(\frac{\chi^2_{0.95}(19)}{\chi^2_{0.05}(19)} - 1\right) = \frac{1}{10{,}816}\left(\frac{30.14}{10.12} - 1\right) = \frac{1.978}{10{,}816} = 1.829\times10^{-4}$$

which corresponds to a relative standard deviation $\xi_D = \sqrt{1.829\times10^{-4}} = 0.01352$, 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

$$F(n) = n\left(\frac{\chi^2_{1-\alpha}(n-1)}{\chi^2_{\beta}(n-1)} - 1\right) \tag{5}$$

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

$$r_0 = \frac{\sum_{i=1}^{n} N_i}{\sum_{i=1}^{n} w_i} \qquad \text{and} \qquad \hat{r} = \sum_{i=1}^{n} \frac{N_i}{1 + r_0 w_i \xi^2} \Big/ \sum_{i=1}^{n} \frac{w_i}{1 + r_0 w_i \xi^2} \tag{6}$$

   (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]

$$\chi^2 = \sum_{i=1}^{n} \frac{(N_i / w_i - \hat{r})^2}{\hat{r} / w_i + \hat{r}^2 \xi^2} \tag{7}$$

5. Determine the quantile $\chi^2_{1-\alpha}(n-1)$ (see Table G.1). 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.

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[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 $N_i + \xi^2 N_i^2$.

The excess component may be estimated by solving Equations 18.6 and 18.7 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

$$\xi^2 = \frac{1}{\overline{N}^2}\left(\frac{1}{n-1}\sum_{i=1}^{n}(N_i - \overline{N})^2 - \overline{N}\right) \tag{8}$$

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

$$\xi^2_{\text{lower}} = \frac{1}{\overline{N}^2}\left(\frac{1}{\chi^2_{(1+\gamma)/2}(n-1)}\sum_{i=1}^{n}(N_i - \overline{N})^2 - \overline{N}\right) \tag{9}$$

and the approximate upper confidence limit is given by

$$\xi^2_{\text{upper}} = \frac{1}{\overline{N}^2}\left(\frac{1}{\chi^2_{(1-\gamma)/2}(n-1)}\sum_{i=1}^{n}(N_i - \overline{N})^2 - \overline{N}\right) \tag{10}$$

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

[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 18.7.

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 18.8 through 18.10 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:

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

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

$$= 0.0096334$$

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

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

$$= 0.022846$$

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.

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 tes 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 $\sum_{i=1}^{n} N_i$ and $\sum_{i=1}^{n} t_i$.

3. Estimate the mean background count rate by

$$\hat{r} = \frac{\sum_{i=1}^{n} N_i}{\sum_{i=1}^{n} t_i} \tag{11}$$

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:

$$\chi^2 = \frac{1}{\hat{r}} \sum_{i=1}^{n} \left(\frac{N_i}{t_i} - \hat{r} \right)^2 t_i \tag{12}$$

6. Determine the quantile $\chi^2_{1-\alpha}(n-1)$ (see Table G.1 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.1, the 0.95-quantile for a chi-square distribution with 19 degrees of freedom is 30.14. Since 18.49 ≤ 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, 1998).

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. I both of the following tests, t denotes the count time, and r denotes the preset lower or upper limi 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

$$Z = \frac{0.5 + N_B - rt}{\sqrt{rt}} \tag{14}$$

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 2NB degrees of freedom (see Table G.1 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.1 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

$$Z = \frac{0.5 + N_B - rt}{\sqrt{rt}} \tag{15}$$

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.1), 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 $N_B \le rt = 60$ and $rt \ge 20$, 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 $-1.226 \ge -1.645$, 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.

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

$$Z = \left(\frac{N_2}{t_2} - \frac{N_1}{t_1} \right) \Big/ \sqrt{\frac{N_1 + N_2}{t_1 t_2}} \qquad (16)$$

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

$$S = \sum_{k=0}^{N_1} \binom{N_1 + N_2}{k} p^k q^{N_1 + N_2 - k} \tag{17}$$

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

$$S = 1 - \sum_{k=N_1+1}^{N_1+N_2} \binom{N_1 + N_2}{k} p^k q^{N_1 + N_2 - k} \tag{18}$$

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 18.17.

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.

18B.5 References

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19 MEASUREMENT STATISTICS

19.1 Overview

This chapter discusses statistical principles and methods applicable to radioanalytical measurements, calibrations, data interpretation, and quality control.

Laboratory measurements always involve uncertainty, which must be considered when analytical results are used as part of a basis for making decisions. Every measured value obtained by a radioanalytical procedure 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.

The uncertainty associated with laboratory measurements is only a part of the total uncertainty that a data user must consider. Field sampling introduces other types of uncertainty, which are beyond the scope of this chapter.

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. An important performance characteristic of an analytical procedure is therefore 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 which will be or could be used. This chapter explains the performance measure, called the "minimum detectable concentration," or in certain cases the "minimum detectable amount," 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 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," which may be used to describe quantification capabilities.

The material in the chapter is arranged so that general information is presented first and the more technical information intended primarily for laboratory personnel is presented last. The general discussion in Sections 19.2 through 19.4 requires little previous knowledge of statistics on the part of the reader and involves no mathematical formulas. Section 19.2 in particular may be

skipped by those familiar with basic statistical concepts. The technical discussion in Sections 19.5 through 19.7 requires an understanding of basic algebra and at least some familiarity with the fundamental concepts of probability and statistics. Attachments 19B–G are intended for technical specialists with stronger mathematical backgrounds. The footnotes also contain information which may be skipped by most readers.

19.2 Statistical Concepts and Terms

19.2.1 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 will most often be the result of a measurement. Random variables will usually be denoted by upper-case letters.

Of primary importance in almost any discussion of a random variable is its *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. Attachment 19A describes several types of distributions, including the following:

- Normal (Gaussian) distributions
- Log-normal distributions
- Chi-square distributions
- Student's *t*-distributions
- Rectangular, or uniform, distributions
- Trapezoidal distributions
- Exponential distributions
- Binomial distributions
- Poisson distributions

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. 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 19.1 and 19.2), because the height of the graph over a point x indicates the probability that the value of X will be near x.

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, $\mathrm{Var}(X)$, 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 dimensions as X. The variance σ_X^2, on the other hand, has the dimensions 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. Two others are the median and the mode. 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 $X \le x_{0.5}$ and the probability that $X \ge x_{0.5}$ are both at least 0.5. The *mode* of X is its most likely value. Figure 19.1 shows the probability density function of a symmetric distribution, whose mean, median, and mode coincide, and Figure 19.2 shows the pdf of an asymmetric distribution, whose mean, median, and mode are distinct.

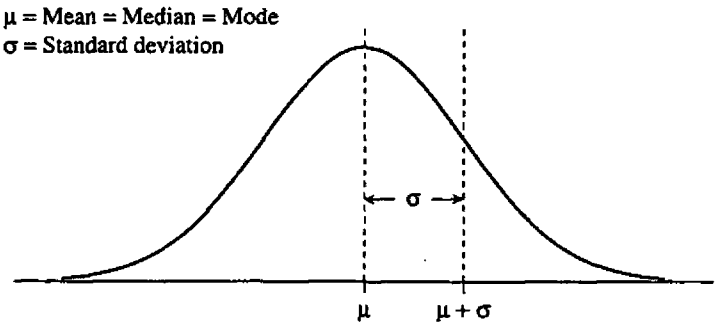

FIGURE 19.1 — A symmetric distribution

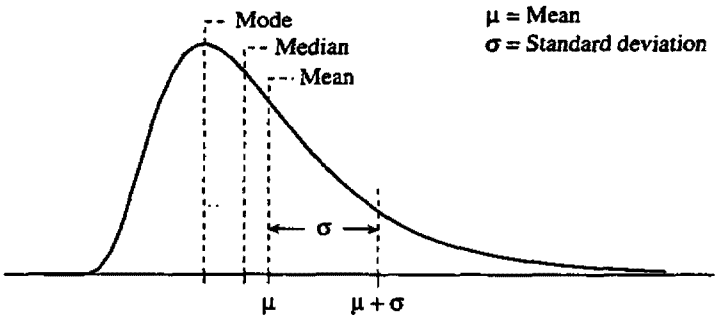

FIGURE 19.2 — An asymmetric distribution

For some distributions, the median or mode may not be unique. If there is a unique mode, the distribution is called *unimodal*; otherwise, it is called *multimodal*.

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 $X \le x_p$ is at least p. A p-quantile is often called a $100p^{th}$ *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 $\mathrm{Cov}(X,Y)$. 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 dimensions. 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. To be more rigorous, X and Y are independent if and only if $\Pr[X \in I \text{ and } Y \in J] = \Pr[X \in I] \cdot \Pr[Y \in J]$ for any intervals I and J in the real line, where the symbol $\in$ denotes set membership.

When the value of a random variable X is used to estimate the value of an unknown parameter p, then X is called an *estimator* for p. The *bias* of X is the difference between the mean μ_X and the actual value p. If the bias is zero, then X is said to be *unbiased*; otherwise, X is *biased*.

19.2.2 Summary of Terms

arithmetic mean: The term "arithmetic mean" denotes the estimate of the expectation of a distribution calculated by dividing the sum of a set of observed values by the number of values. It is also called the "average."

bias: If X is an estimator for a parameter p, then the *bias* of X is $\mu_X - p$.

coefficient of variation: The *coefficient of variation* of a nonnegative distribution is the ratio of its standard deviation to its mean.

correlated: Two random variables are *correlated* if their covariance is nonzero.

correlation coefficient: The *correlation coefficient* of two random variables is equal to their covariance divided by the product of their standard deviations.

covariance: The *covariance* of two random variables X and Y, denoted by $\mathrm{Cov}(X,Y)$ or $\sigma_{X,Y}$, is a measure of the association between them, and is defined as $E[(X - \mu_X)(Y - \mu_Y)]$.

distribution: 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 function: The *distribution function*, or *cumulative distribution function*, of a random variable X is the function F defined by $F(x) = \Pr[X \le x]$.

estimator: A random variable whose value is used to estimate an unknown parameter p is called an *estimator* for p.

expectation: The *expectation* of a random variable X, denoted by $E(X)$ or μ_X, is a measure of the center of its distribution and is defined as a probability-weighted average of the possible numerical values.

expected value: See *expectation.*

independent: A collection of random variables $X_1, X_2, \ldots, X_n$ is *independent* if $\Pr[X_1 \in I_1, X_2 \in I_2, \ldots, X_n \in I_n] = \Pr[X_1 \in I_1] \cdot \Pr[X_2 \in I_2] \cdots \Pr[X_n \in I_n]$ for all intervals $I_1, I_2, \ldots, I_n$ in the real line.

mean: See *expectation.*

median: 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.

mode: The *mode* of a distribution is its most probable value.

percentile: A $100p^{th}$ *percentile* of X is the same as a p-quantile of X.

probability density function (pdf): 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.

quantile: 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 $X \le x_p$ is at least p.

random variable: A *random variable* is the numerical outcome of an experiment which produces varying results when repeated.

relative standard deviation (RSD): See *coefficient of variation.*

relative variance: The *relative variance* of a random variable is the square of the coefficient of variation.

standard deviation: 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 square root of the variance of X.

variance: The *variance* of a random variable X, denoted by σ_X^2, Var(X), or $V(X)$, is defined as $E[(X - \mu_X)^2]$.

19.3 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.

19.3.1 Measurement, Error, and Uncertainty

The result of a measurement is generally used to estimate some physical quantity called the *measurand*. For example, the measurand for a radioactivity measurement might be the activity concentration of ^{238}Pu in a laboratory sample. The measured result may vary with each repetition

of the measurement and should therefore be considered a random variable. The difference between the measured result and the actual value of the measurand is the *error* of the measurement, which is also a random variable.

Measurement error may be caused by *random effects* or *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*. 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 concentration 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.

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 activities.

The error of a measurement is primarily a theoretical concept, because its value is unknowable. The *uncertainty* of a measurement, however, 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 estimate of the uncertainty is required for every measured result.

19.3.2 The Measurement Process

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 neces-

sary for the intended purpose of the data.[1] For example, when measuring the concentration of a radionuclide in a laboratory sample, it is generally necessary to specify the concentration 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., concentration per unit volume of liquid 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, instrument background count, counting efficiency, and test portion size. The second step in defining the measurement process is therefore to determine the mathematical model for the relationship between the measurand Y and measurable input quantities X_i on which its value depends. The relationship may be a simple functional relationship, expressible as $Y = f(X_1, X_2, \ldots, X_N)$, or it may happen that Y is most conveniently expressed as the simultaneous solution of a set of equations.

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 concentration) may be the product of factors such as the mass of the test portion, the chemical yield, 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 $y = f(x_1, x_2, \ldots, x_N)$.[2] Since there is an uncertainty in each *input estimate*, x_i, there is also an uncertainty in the *output estimate*, 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.

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[1] 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."

[2] In accordance with the *GUM*, an uppercase Roman 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.

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 a standard deviation, called the *standard uncertainty* and denoted by $u(x_i)$, or in the form of a 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. 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 ISO terminology.) The square of the combined standard uncertainty, denoted by $u_c^2(y)$, is called the *combined variance.*

The process of combining the standard uncertainties of the input estimates x_i 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 19.5.

Methods for evaluating the standard uncertainties $u(x_i)$ are classified as either Type A or Type B. A *Type A* evaluation of a standard uncertainty $u(x_i)$ may be performed by making a series of independent measurements of the quantity x_i and calculating the arithmetic mean and 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 counting model, which is the mathematical basis for this rule, is discussed in Section 19.6. 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 for all sources believed to be potentially significant in the final result.

19.3.6 Expanded Uncertainty

The laboratory 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 uncer-

tainty 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 determined accurately, 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 is determined accurately. Attachment 19C 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 estimate of $u_c(y)$.

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). MARLAP recommends this convention and suggests that uncertainties be rounded to two figures. The following examples demonstrate the application of the rule.

EXAMPLES

MEASURED VALUE (y)	EXPANDED UNCERTAINTY $U = ku_c(y)$	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 19.6.10 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. 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). One 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 the approximate coverage probability. A complete report should also describe the methods used to calculate the uncertainties.

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 19C of this chapter.)

19.3.9 Recommendations

MARLAP makes the following recommendations.

- 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.
- Each measured value should be reported with either its combined standard uncertainty or its expanded uncertainty.
- The reported measurement uncertainties should be clearly explained. In particular, the coverage factor and approximate coverage probability should be stated whenever an expanded uncertainty is reported.
- A laboratory should consider all possible sources of measurement uncertainty and evaluate and propagate the uncertainties for all sources believed to be potentially significant in the final result.
- Each uncertainty should be rounded to two significant figures, and the measured value should be rounded to the same number of decimal places as its uncertainty.
- All results, whether positive, negative, or zero, should be reported as obtained, together with their uncertainties.

19.3.10 Summary of Terms

blunder: mistake made by a person performing a measurement.

combined standard uncertainty: standard uncertainty of an output estimate calculated by combining the standard uncertainties of the input estimates. The combined standard uncertainty of y is denoted by $u_c(y)$.

combined variance: the square of the combined standard uncertainty. The combined variance of y is denoted by $u_c^2(y)$.

counting error: See *counting uncertainty*. MARLAP uses the term "counting uncertainty" to maintain a clear distinction between the concepts of measurement error and uncertainty.

counting uncertainty: component of measurement uncertainty caused by the random nature of radioactive decay and radiation counting.

coverage factor: value k multiplied by the combined standard uncertainty $u_c(y)$ to give the expanded uncertainty U.

coverage probability: approximate probability that the reported interval will contain the value of the measurand.

error (of measurement): difference between a measured result and the value of the measurand (cf. uncertainty of measurement).

expanded uncertainty: 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 Y.

***GUM*:** abbreviation used in this chapter for the *Guide to the Expression of Uncertainty in Measurement* (ISO 1995).

input estimate: measured value of an input quantity.

input quantity: 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*.

level of confidence: See *coverage probability*.

measurand: quantity subject to measurement.

output estimate: calculated value of an output quantity.

output quantity: the quantity in a mathematical measurement model whose value is calculated from the measured values of other quantities in the model.

random effect: any effect in a measurement process which causes the measured result to vary randomly when the measurement is repeated.

random error: a measurement error which varies randomly when the measurement is repeated — caused by random effects.

relative standard uncertainty: the ratio of the standard uncertainty of a measured result to the result itself. The relative standard uncertainty of x may be denoted by $u_r(x)$.

sigma (σ): 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. The symbol σ and the term "sigma" are more properly used to denote a true standard deviation.

spurious error: a measurement error caused by a human blunder, instrument malfunction, or other unexpected or abnormal event

standard uncertainty: uncertainty of a measured value expressed as a standard deviation — often called a "1-sigma" uncertainty. The standard uncertainty of x is denoted by $u(x)$.

systematic effect: any effect in a measurement process which does not vary randomly when the measurement is repeated.

systematic error: a measurement error which does not vary randomly when the measurement is repeated — caused by systematic effects.

total propagated uncertainty (TPU): See *combined standard uncertainty*, which is the preferred term.

Type A evaluation: experimental evaluation of a standard uncertainty or covariance using repeated measurements.

Type B evaluation: evaluation of a standard uncertainty or covariance by a method that is not a Type A method.

uncertainty (of measurement): "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 propagation: 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.

19.4 Detection and Quantification Capability

19.4.1 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.

Hypothesis testing has been used for analyte detection in radiochemistry since at least 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 two-part standard which deals with issues of detection in an even more general context of measurement (ISO 1997). Part 1 of ISO 11843 includes terms and definitions. Part 2, which is not available at the time of this writing, will 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" (ISO 2000a–c). 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. Blank 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 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.)

A detection decision requires a choice between two hypotheses about the material being analyzed. The first hypothesis is the "null hypothesis" H_0: The analyte concentration of the material is no greater than that of the blank (i.e., the material is in the basic state). The second hypothesis is the "alternative hypothesis" H_1: The analyte concentration of the material is greater than that of the blank. The choice between the two hypotheses is based on 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. 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 the probability α that the null hypothesis will be rejected in a situation where it is in fact true (i.e., a "type I error," or "false positive"). The significance level α is usually chosen to be 0.05. This means that when a blank sample is analyzed, there is a 5% probability of incorrectly deciding that the analyte is present. A smaller value of α makes type I errors less likely, but also makes type II errors ("false negatives") more likely when the laboratory sample concentration is near the blank concentration.

The term "blank" here may mean any of several types of blanks, including instrument blanks (or backgrounds) and reagent blanks. The blank is chosen to provide an estimate of the mean signal produced by an actual sample that contains none of the analyte, whether the signal is produced by the instrument background, contaminated reagents, or other causes.

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 19.3.2.

The *critical value of the analyte concentration* x_C, according to the ISO definition, 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 this formula typically involves division by the counting efficiency, test portion size, chemical yield, decay factor, and possibly other factors. In ANSI N42.23, the same value x_C is called the *decision level concentration*, or DLC (ANSI 1996b).

According to ISO 11843-1, a detection decision involves the critical value of the response variable, or gross instrument signal, which, in a radioactivity measurement, is typically a total count or count rate. However, it has become standard practice in radioanalysis to use instead the critical value of the *net* instrument signal, which is calculated from the gross signal by subtracting the estimated blank value and any interferences. This practice is consistent with the recommendations of IUPAC (1995), where the critical value of the net instrument signal S is denoted by S_C. 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 count, or the critical (value of the) gross count.

Section 19.7.1 and Section 19D.2 of Attachment 19D provide more information on the calculation of critical values.

19.4.2 The Minimum Detectable Concentration

The *minimum detectable concentration* is the concentration of analyte that must be present in a laboratory sample to give a specified probability $1 - \beta$ of detection. Then β is the probability of failing to reject the null hypothesis when it is false (i.e., a "type II error," or "false negative"). The minimum detectable concentration is often abbreviated as MDC. In the ISO terminology the MDC is called the *minimum detectable value of the net state variable*, denoted by x_D, which is defined as the smallest (true) value of the net state variable that gives a specified high probability $1 - \beta$ that the value of the response variable will exceed its critical value, thus leading one to conclude correctly that the material analyzed is not in the basic state (i.e., the material is not blank). The relationship between the critical value and the minimum detectable value of the net state variable is shown in Figure 19.3.

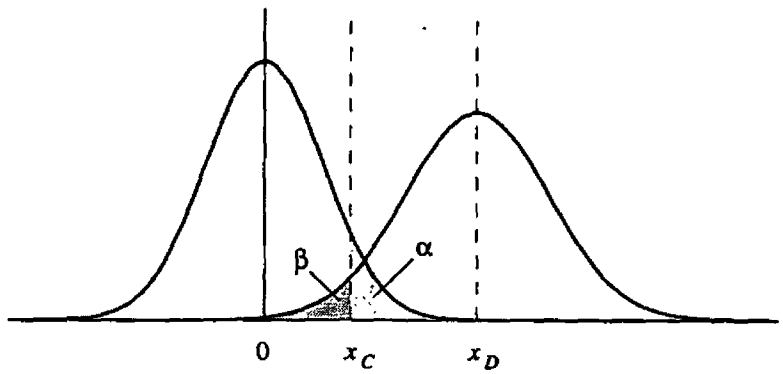

FIGURE 19.3 — The critical value x_C and minimum detectable value x_D of the net state variable

Sections 19.7.2 and 19D.3 provide more information about the calculation of the minimum detectable concentration.

When the quantity being measured is the total amount of analyte in an item and not an analyte concentration, the minimum detectable value is sometimes called the *minimum detectable amount*, which may be abbreviated as MDA. This chapter focuses on the MDC, but with few changes the guidance is also applicable to the 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 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 not defensible.

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 performed. 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.

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. The nominal MDC for the measurement process is a constant — *not* a random variable.

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.

19.4.3 Differences between the ISO and IUPAC Definitions

The ISO and IUPAC guidance documents give different definitions for some of the terms listed above and promote somewhat different concepts. In general, the IUPAC approach is to define the "critical value" and "minimum detectable value" separately for the signal and concentration domains. A detection decision may be made in either domain, but the outcome of the decision may depend on which domain is chosen. With the ISO approach the outcome does not depend on the domain. Either domain may be chosen, but *in effect* all detection decisions are made in the signal domain.

The IUPAC and ISO approaches to detection in the signal domain, although expressed differently, are effectively equivalent. (IUPAC bases detection decisions on the net signal S, whereas ISO bases detection decisions on the gross signal Y.) The more important differences are in the concentration domain (X). For example, according to IUPAC, the critical analyte concentration x_C is determined from the distribution of the measured concentration X, taking into account its overall measurement uncertainty. According to ISO, x_C is simply a function of y_C, the critical value of the response variable. Since x_C is related to y_C in the same way that X is related to Y, it makes no difference whether detection decisions are based on X or Y — the outcome is the same.

The IUPAC guidance defines the minimum detectable concentration x_D as the smallest concentration that gives a specified high probability of obtaining a measured concentration greater than x_C, which is inconsistent with the ISO guidance because of the differing definitions of x_C.

One consequence of the IUPAC definitions is that the measurement variances of sensitivity factors such as the test portion size, counting efficiency, and chemical yield increase the values of x_C and x_D because they increase the variance of X. According to the ISO definitions, these variances do not increase the values of x_C and x_D, although they generate uncertainties in the estimates of x_C and x_D. In principle, the ISO definitions imply that variability in the true values of these sensitivity factors *does* increase x_D, although the draft implementation guidance in ISO 11843-2 apparently does not deal with the issue.

As stated above, MARLAP adopts the ISO definitions but also follows the IUPAC guidance where it does not contradict the definitions of ISO 11843-1. The draft implementation guidance in ISO 11843-2 appears not to be designed for typical radioanalytical measurement processes.

19.4.4 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 "MDC" 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.

The similarity between the abbreviations MDC and MDL tends to produce confusion. The term "method detection limit" is seldom used in the context of radioanalysis 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.

19.4.5 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 19.7.3 provides more information about the calculation of the minimum quantifiable concentration.

Historically much attention has been given to the detection capabilities of radioanalytical 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 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).

[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.

19.4.6 Recommendations

MARLAP makes the following recommendation.

- A measurement result should not be compared to the minimum detectable concentration to make an analyte detection decision. A detection decision may be made by comparing the gross signal, net signal, or measured analyte concentration to its corresponding critical value.

19.4.7 Summary of Terms

basic state: in radiochemistry, the chemical composition of blank material.

critical level: See *critical value*.

critical value: in the context of analyte detection, the minimum value of the response variable (or the measured analyte concentration) required to give confidence that a positive amount of analyte is present in the material analyzed.

decision level: See *critical value*.

detection limit: See *minimum detectable value*.

false negative: See *type I decision error*. This chapter avoids the terms "false negative" and "false positive," because they may be confusing in some contexts.

false positive: See *type II decision error*.

lower limit of detection (LLD): (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% probability with no greater than a 5% 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).

method detection limit (MDL): "the minimum concentration of a substance that can be measured and reported with 99% 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).

minimum detectable amount (MDA): the minimum detectable value of the total amount of analyte in the sample being analyzed.

minimum detectable concentration (MDC): the minimum detectable value of the analyte concentration in a laboratory sample.

minimum detectable value: the smallest value of the net state variable (amount or concentration of analyte) that ensures a specified high probability $1 - \beta$ of detection.

minimum quantifiable concentration (MQC): the minimum quantifiable value of the analyte concentration in a laboratory sample.

minimum quantifiable value: the smallest value of the net state variable (analyte amount or concentration) that ensures the relative standard deviation of the measurement is not greater than a specified value, usually 10%.

net state variable (X): the difference between the state variable Z and its value in the basic state —in radiochemistry, usually equal to Z, because the value of Z in the basic state is zero.

quantification limit: See *minimum quantifiable value*.

response variable (Y): the variable that gives the observable result of a measurement—in radiochemistry, typically a gross count or count rate.

significance level (α): in a hypothesis test, the probability of a type I decision error.

state variable (Z): the quantity that describes the state of the material analyzed—in radiochemistry, usually the analyte activity concentration.

type I decision error: in a hypothesis test, the error made by rejecting the null hypothesis when it is true (a "false positive").

type II decision error: in a hypothesis test, the error made by failing to reject the null hypothesis when it is false (a "false negative").

19.5 Procedures for Estimating Uncertainty

The steps for evaluating and reporting the uncertainty of a radioactivity 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 Sections 19.3.2 and 19.3.9).

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 19.5.2).

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 19.5.3).

7. 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 19C).

8. Report the result as $y \pm U$ with the unit of measure, and, at a minimum, state the coverage factor used to compute U and the estimated coverage probability.

19.5.1 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. In particular, counting uncertainty, pipetting and weighing uncertainties, and uncertainties in standard concentrations should always be evaluated. Other possible causes of uncertainty include source geometry and placement, variable instrument backgrounds and efficiencies, time measurements used in decay and ingrowth calculations, instrument dead-time corrections, approximation errors in simplified mathematical models, impurities in reagents, and uncertainties in the published values for half-lives and radiation emission probabilities.

19.5.2 Evaluation of Standard Uncertainties

Calculating the combined standard uncertainty of an output estimate $y = f(x_1, x_2, \ldots, x_N)$ requires the estimation 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.

19.5.2.1 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

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

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 $\sqrt{n}$.

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

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

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

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

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

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

783 **EXAMPLE**: Ten independent measurements of a quantity X_i are made, yielding the values

784 12.132 12.139 12.128 12.133 12.132
785 12.135 12.130 12.129 12.134 12.136

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

787 $$x_i = \overline{X}_i = \frac{1}{n} \sum_{k=1}^{n} X_{i,k} = \frac{121.328}{10} = 12.1328$$

788 The standard uncertainty of x_i is

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

789

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

$$= \sqrt{1.12888 \times 10^{-6}} \quad = 0.0011$$

790 If X_i and X_j are two input quantities and estimates of their values are correlated, a Type A evalua-
791 tion of covariance may be performed by making n independent pairs of simultaneous observa-
792 tions of X_i and X_j and calculating the experimental covariance of the means. If the observed pairs
793 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

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

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

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

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

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

796 An evaluation of variances and covariances of parameters determined by the method of least
797 squares may also be a Type A evaluation (see Attachment 19B).

798 19.5.2.2 Type B Evaluations

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

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

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

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

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

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

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

816 **EXAMPLE**: A strontium carrier solution is prepared by dissolving strontium nitrate in acidified
817 water. The purity, P, of the strontium nitrate is stated to be 99.9%, or 0.999, but no tolerance
818 or uncertainty is provided. By default, a rectangular distribution with half-width $1 - P$, or
819 0.001, is assumed. So, the standard uncertainty of P is evaluated as $u(P) = 0.001 / \sqrt{3} =$
820 0.00058.

If the value of x is believed to lie between a lower bound a_- and an upper bound a_+, but values near these two bounds are considered less likely than those near the midpoint, then a symmetric *trapezoidal* distribution may be used to obtain the input estimate and its standard uncertainty (see Section 19A.7 in Attachment 19A). If the ratio of the width of the trapezoid at its top to the width at its base is β, where $0 < \beta < 1$, then the input estimate is the midpoint $x = (a_- + a_+) / 2$, and its standard uncertainty is

$$u(x) = \frac{(a_+ - a_-)}{2}\sqrt{\frac{1+\beta^2}{6}} \qquad (19.9)$$

As β approaches zero, the trapezoidal distribution becomes *triangular*. As β approaches one, the trapezoidal distribution becomes rectangular.

EXAMPLE: 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 distribution with $a_- = 34.3$, $a_+ = 34.5$, and $\beta = (34.45 - 34.35) / (34.5 - 34.3) = 0.5$, one obtains the input estimate $x = 34.4$ and the standard uncertainty $u(x) = \frac{34.5 - 34.3}{2}\sqrt{\frac{1 + 0.5^2}{6}} = 0.046$.

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: The uncertainty for a measured concentration x is stated to be 0.015 Bq g^{-1} and the stated multiplier is 2. So, the standard uncertainty of x is $u(x) = 0.015 / 2 = 0.0075$ Bq g^{-1}.

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 $100\gamma\%$ 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

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

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

844 **EXAMPLE**: The activity concentration x of a commercial standard solution is stated to lie
845 within the interval 4530 ± 64 Bq g^{-1} with 95% confidence. The standard uncertainty may
846 therefore be evaluated as $u(x) = 64 / z_{0.975} = 64 / 1.96 = 33$ Bq g^{-1}.

847 **19.5.3 Combined Standard Uncertainty**

848 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
849 input quantities X_i and $y = f(x_1, x_2, \ldots, x_N)$ is the calculated value of the measurand Y, the variance
850 of y is estimated using the following formula.

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

The Uncertainty Propagation Formula

851 Here $u^2(x_i)$ denotes the estimated variance of x_i, or the square of its standard uncertainty; $u(x_i, x_j)$
852 denotes the estimated covariance of x_i and x_j; $\partial y / \partial x_i$ (or $\partial f / \partial x_i$) denotes the partial derivative of
853 Y with respect to X_i evaluated at the measured values $x_1, x_2, \ldots, x_N$; and $u_c(y)$ denotes the com-
854 bined standard uncertainty of y. The partial derivatives $\partial y / \partial x_i$ are called *sensitivity coefficients*.

855 The preceding formula, called the "law of propagation of uncertainty" in the *GUM*, will be called
856 the "uncertainty propagation formula" in this document.

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

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

859 Equation 19.12 is only valid when the input estimates are uncorrelated. Although this case occurs
860 frequently in practice, there are notable exceptions. When input estimates are obtained using the
861 same measuring devices or the same standard solutions, or when they are calculated from the
862 same data, there is a potential for correlation. For example, instrument calibration parameters
863 determined by least-squares analysis may be strongly correlated. Fortunately, the method of least

TABLE 19.1 — Applications of the 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 $$u_c^2(e^{ax}) = a^2e^{2ax}u^2(x)$$ If n is a positive integral constant, then $$u_c^2(x^n) = n^2x^{2n-2}u^2(x)$$ If x is positive, then $$u_c^2(x^y) = x^{2y}\left(\frac{y^2u^2(x)}{x^2} + (\ln x)^2u^2(y) + \frac{2y(\ln x)u(x,y)}{x}\right)$$
LOGARITHMS	If a is a constant and ax is positive, then $$u_c^2(\ln ax) = \frac{u^2(x)}{x^2} \quad \text{and} \quad u_c^2(\log_{10} ax) = \frac{u^2(x)}{(\ln 10)^2x^2} \approx \frac{u^2(x)}{5.302 \cdot x^2}$$

squares provides covariance estimates with almost no additional effort (see Attachment 19B). In general, ignoring correlations between the input estimates may lead to overestimation or underestimation of the combined standard uncertainty.

Table 19.1 shows how to propagate uncertainties in some common cases.

The product of $|\partial y / \partial x_i|$ and the standard uncertainty $u(x_i)$ is called the *component* of the combined standard uncertainty $u_c(y)$ *generated by* the standard uncertainty of x_i, and may be

870 denoted by $u_i(y)$. When all the input estimates are uncorrelated, the combined standard uncer-
871 tainty may be written in terms of its components as follows.

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

872 Since $u_c^2(y)$ is the sum of the squares of the components $u_i(y)$, the combined standard uncertainty
873 tends to be determined primarily by its largest components.

874 **EXAMPLE**

875 **Problem**: A 6000-s gross alpha measurement is performed on a test source prepared by evap-
876 orating water on a stainless steel planchet. The measurement produces 120 alpha counts. The
877 preceding background measurement on the instrument had a duration of 6000 s and produced
878 42 alpha counts. The estimated alpha counting efficiency is 0.223 with a standard uncertainty
879 of 0.015. The sample volume analyzed is 0.05000 L, with a standard uncertainty of 0.00019 L.
880 The alpha emission rate per unit volume is described by the mathematical model

881 $$A = \frac{N_S / t_S - N_B / t_B}{\varepsilon V}$$

882 where

883 N_S is the source count ($N_S = 120$)
884 N_B is the background count ($N_B = 42$)
885 t_S is the source count time ($t_S = 6000$)
886 t_B is the background count time ($t_B = 6000$)
887 ε is the counting efficiency ($\varepsilon = 0.223$)
888 V is the volume analyzed ($V = 0.0500$)

889 What is the output estimate A and what is its combined standard uncertainty, $u_c(A)$?

890 **Solution**: First compute the output estimate A (alphas per second per liter).

891 $$A = \frac{N_S / t_S - N_B / t_B}{\varepsilon V} = \frac{120/6000 - 42/6000}{(0.223)(0.05000)} \approx 1.17$$

Then compute the combined standard uncertainty $u_c(A)$. 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

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

The partial derivatives are evaluated as follows:

$$\frac{\partial A}{\partial N_S} = \frac{1}{t_S \varepsilon V} \approx 0.0149477 \qquad \frac{\partial A}{\partial N_B} = \frac{-1}{t_B \varepsilon V} = -0.0149477$$

$$\frac{\partial A}{\partial \varepsilon} = -\frac{N_S/t_S - N_B/t_B}{\varepsilon^2 V} = -5.22834 \qquad \frac{\partial A}{\partial V} = -\frac{N_S/t_S - N_B/t_B}{\varepsilon V^2} = -23.3184$$

The Poisson model 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 $u_c^2(A) = 0.0424$; so, the combined standard uncertainty is $u_c(A) = \sqrt{0.0424} \approx 0.21$.

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

$$u_c^2(y) = y^2 \left(\frac{u^2(x_1)}{x_1^2} + \frac{u^2(x_2)}{x_2^2} + \cdots + \frac{u^2(x_n)}{x_n^2} + \frac{u^2(z_1)}{z_1^2} + \frac{u^2(z_2)}{z_2^2} + \cdots + \frac{u^2(z_m)}{z_m^2} \right) \qquad (19.14)$$

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

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

Equation 19.15 is particularly useful in radioanalysis, 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: Consider the preceding gross-alpha example. Equation 19.15 implies the following equation for the combined variance of A.

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

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

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

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

19.5.4 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

$$u(y,z) = \sum_{i=1}^{N} \sum_{j=1}^{N} \frac{\partial y}{\partial x_i} \frac{\partial z}{\partial x_j} u(x_i, x_j) \tag{19.16}$$

Since $u(y,y) = u_c^2(y)$, the preceding equation may be considered a generalization of the uncertainty propagation formula.[4]

19.5.5 Nonlinear Models

19.5.5.1 Uncertainty Propagation

The 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 uncertainty propagation 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.[5] In radiochemistry this rule applies, for example, to the uncertainty of an instrument calibration factor, chemical yield, or test portion size.

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.

---

[4] The uncertainty propagation formula may also be generalized using the matrix notation of Attachment 19B. If $y = f(x)$, where x and y are column vectors and f is a vector-valued function, then

$$\mathbf{u}^2(y) = \left(\frac{\partial f}{\partial x}\right) \mathbf{u}^2(x) \left(\frac{\partial f}{\partial x}\right)'$$

This formula describes how the variances and covariances of the vector components of y are related to the variances and covariances of the vector components of x. When y has only one component, the formula here is equivalent to the uncertainty propagation formula.

[5] 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.

$$u_c^2(y) = \sum_{i=1}^{N} \left(\frac{\partial y}{\partial x_i} \right)^2 u^2(x_i) + \sum_{i=1}^{N} \sum_{j=1}^{N} \left(\frac{1}{2} \left(\frac{\partial^2 y}{\partial x_i \partial x_j} \right)^2 + \frac{\partial y}{\partial x_i} \frac{\partial^3 y}{\partial x_i \partial x_j^2} \right) u^2(x_i) u^2(x_j) \qquad (19.17)$$

941 See also Section 5.1.2 of the *GUM*.

942 **EXAMPLE:** Suppose x and y are independent estimates of input quantities X and Y, respec-
943 tively. Then the combined variance of the product $p = xy$ according to the (first-order)
944 uncertainty propagation formula is

945 $$u_c^2(p) = y^2 u^2(x) + x^2 u^2(y)$$

946 For example, suppose $x = 5$, with $u(x) = 0.5$, and $y = 10$, with $u(y) = 1$. Then $p = 50$, and the
947 first-order formula gives the combined standard uncertainty

948 $$u_c(p) = \sqrt{10^2 0.5^2 + 5^2 1^2} = 7.07$$

949 When higher-order terms are included,

950 $$u_c^2(p) = y^2 u^2(x) + x^2 u^2(y) + 0 \cdot u^4(x) + \frac{1}{2} u^2(x) u^2(y) + \frac{1}{2} u^2(y) u^2(x) + 0 \cdot u^4(y)$$
$$= y^2 u^2(x) + x^2 u^2(y) + u^2(x) u^2(y)$$

951 With numbers,

952 $$u_c(p) = \sqrt{10^2 0.5^2 + 5^2 1^2 + 0.5^2 1^2} = 7.09$$

953 The combined variance of the quotient $q = x / y$ according to the first-order formula is

954 $$u_c^2(q) = \frac{u^2(x)}{y^2} + q^2 \frac{u^2(y)}{y^2}$$

955 Using the same values for x and y again, $q = 0.5$ and the first-order formula gives

956
$$u_c(q) = \sqrt{\frac{0.5^2}{10^2} + 0.5^2 \frac{1^2}{10^2}} = 0.0707$$

957 When the higher-order terms are included,

958
$$\frac{\partial q}{\partial x} = \frac{1}{y} \qquad \frac{\partial^2 q}{\partial x^2} = 0 \qquad \frac{\partial^3 q}{\partial x^3} = 0$$

$$\frac{\partial q}{\partial y} = -\frac{x}{y^2} \qquad \frac{\partial^2 q}{\partial y^2} = \frac{2x}{y^3} \qquad \frac{\partial^3 q}{\partial y^3} = -\frac{6x}{y^4}$$

$$\frac{\partial^2 q}{\partial x\,\partial y} = -\frac{1}{y^2} \qquad \frac{\partial^3 q}{\partial x\,\partial y^2} = \frac{2}{y^3} \qquad \frac{\partial^3 q}{\partial y\,\partial x^2} = 0$$

959
$$u_c^2(q) = \frac{u^2(x)}{y^2} + q^2 \frac{u^2(y)}{y^2} + 0 \cdot u^4(x) + \left(\frac{1}{2}\left(-\frac{1}{y^2} \right)^2 + \left(\frac{1}{y} \right)\left(\frac{2}{y^3} \right) \right) u^2(x)\, u^2(y)$$
$$+ \left(\frac{1}{2}\left(-\frac{1}{y^2} \right)^2 + 0 \right) u^2(y)\, u^2(x) + \left(\frac{1}{2}\left(\frac{4x^2}{y^6} \right) + \left(-\frac{x}{y^2} \right)\left(-\frac{6x}{y^4} \right) \right) u^4(y)$$
$$= \frac{u^2(x)}{y^2}\left(1 + 3\frac{u^2(y)}{y^2} \right) + q^2 \frac{u^2(y)}{y^2}\left(1 + 8\frac{u^2(y)}{y^2} \right)$$

960 With numbers,

961
$$u_c(q) = \sqrt{\frac{0.5^2}{10^2}\left(1 + 3\frac{1^2}{10^2} \right) + 0.5^2 \frac{1^2}{10^2}\left(1 + 8\frac{1^2}{10^2} \right)} = 0.0726$$

962 19.5.5.2 Bias

963 If f is nonlinear, its nonlinearity may also tend to bias the output estimate y. The bias may be esti-
964 mated, if necessary, by the formula

$$\text{Bias}(y) \approx \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}\frac{\partial^2 y}{\partial x_i \partial x_j}u(x_i,x_j) \tag{19.18}$$

which, in practice, is equivalent to

$$\text{Bias}(y) \approx \frac{1}{2}\sum_{i=1}^{N}\frac{\partial^2 y}{\partial x_i^2}u^2(x_i) + \sum_{i=1}^{N-1}\sum_{j=i+1}^{N}\frac{\partial^2 y}{\partial x_i \partial x_j}u(x_i,x_j) \tag{19.19}$$

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.

EXAMPLE: 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 19.19. 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 $\text{Bias}(y) \approx (1/2)(2x^{-3})u^2(x) = u^2(x)/x^3$. The combined variance of y given by the uncertainty propagation formula is $u_c^2(y) = (-x^{-2})^2 u^2(x) = u^2(x)/x^4$. So, the ratio of the bias to the combined standard uncertainty can be estimated as $(u^2(x)/x^3) / (u(x)/x^2) = u(x)/x$, which is approximately the same as the relative standard uncertainty of x. Therefore, the size of the relative standard uncertainty gives an indication of the practical significance of the bias.

EXAMPLE: If x and y are uncorrelated 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 $\partial^2 z / \partial x^2 = \partial^2 z / \partial y^2 = 0$.

EXAMPLE: 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. 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

$$\frac{1}{2}(0.112707)^2(2)^2 = 0.025$$

or 2.5%. Note that the relative bias of d is small if $u^2(t) / t_{1/2}^2$ is small.

19.5.5.3 Nominal Values

Sometimes an input estimate x_i is a nominal value and not the result of a measurement. This may be true for example when an analyst uses a pipet to dispense a predetermined amount of tracer into a sample. In this case the input estimate x_i is the predetermined volume. Since x_i never varies, its variance is zero, but the volume of liquid dispensed varies each time the measurement is repeated. So, the final result does have a variance component associated with the pipet. If the tracer is used to measure the yield for a chemical separation, the value x_i appears as a factor in the denominator of a mathematical expression, but the variable factor in that expression is actually the count rate produced by the tracer, which appears in the numerator. The variance of this count rate is increased by the variability of the tracer volume. The first-order uncertainty propagation formula gives the same result for the uncertainty of the yield regardless of whether the nominal value or the true value is assumed to be variable, but the higher-order formula may not.

When nominal values appear in the calculation, one must also be careful when applying the bias formula. For example, the quotient x / y may by biased if y is the result of a measurement, but it is not inherently biased if y is a nominal value.

EXAMPLE: Suppose the measurement model is

$$X = \frac{Y - B}{a}$$

where Y is the gross signal, B is the blank signal, and a is the nominal value for a randomly varying sensitivity factor A, whose true value is always unknown. Suppose Y can be written in the form $Y = xA + b + \varepsilon_Y$; where x is the true value of the measurand; b is the true blank level; and ε_Y denotes the measurement error of Y. If all the measured (and nominal) values are unbiased (i.e., if $E(A) = a$, $E(B) = b$, and $E(\varepsilon_Y) = 0$), then the mean of X is given by

$$E(X) = \frac{E(Y) - E(B)}{a} = \frac{(xa + b + 0) - b}{a} = x$$

So, X is an *unbiased* estimator for x. If one treats a as a random variable, this chapter's bias-approximation formula gives the incorrect value $Xu^2(a) / a^2$ for the bias of X.

Assume A, B, and ε_Y are uncorrelated. Then the variance of Y is the sum of two components $\sigma^2_{\varepsilon_Y}$ and $x^2\sigma^2_A$, which may be estimated by $u^2(\varepsilon_Y)$ and $X^2u^2(a)$, respectively, where $u^2(a)$ is actually an estimate of the variance of A. The combined variance of X is given by

$$u_c^2(X) = \frac{u^2(Y) + u^2(B)}{a^2} = \frac{u^2(\varepsilon_Y) + X^2u^2(a) + u^2(B)}{a^2}$$

The expression on the right may be obtained from the first-order uncertainty propagation formula even if one incorrectly treats a as a random variable and A as a constant, so that $u^2(Y) = u^2(\varepsilon_Y)$. If the higher-order approximation is used, the same expression is obtained only if one correctly treats a as the constant and A as the random variable.

19.6 Radiation Measurement Uncertainty

19.6.1 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 19.4.

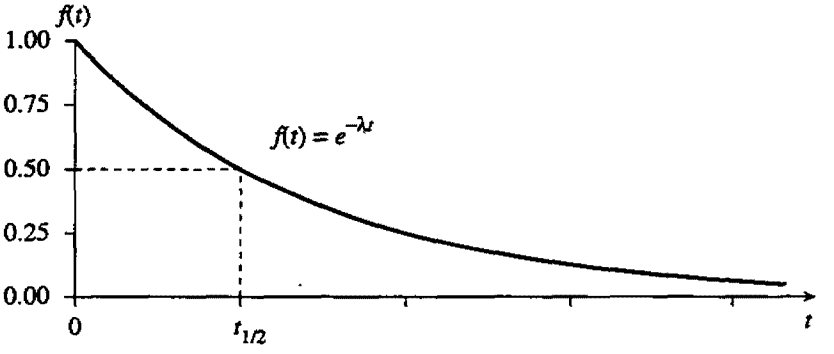

FIGURE 19.4 — Expected fraction of atoms remaining at time t

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 $1 - e^{-\lambda t}$.

19.6.2 Radiation Counting

Undoubtedly the best-known rule of radiation measurement statistics is the fact that the counting uncertainty for a gross radioactivity 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.

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 (nuclear transformation), 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 $1 - e^{-\lambda t}$, where λ is the decay constant and t 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 same as the counting efficiency ε. Then the probability that an atom will generate a count is $p = (1 - e^{-\lambda t})F\varepsilon$.

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.*

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. 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 $\sqrt{N}$.[6]

---

[6] In the rare cases when the Poisson counting 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 a Poisson background is measured for time t_B and N_B counts are observed, the standard deviation of N_S should be estimated instead by

$$\sigma_{N_S} \approx \sqrt{(1-p)N_S + pN_B\frac{t}{t_B}}$$

These two expressions are appropriate only when the source counts are generated by a single radionuclide or by one radionuclide plus the instrument background.

When μ is large, $\sqrt{N}$ is an excellent estimator for the standard deviation, 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 is negligible. 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 19C).[7]

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, but 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 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 counting 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.[8]

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 a series of short-lived progeny (Lucas and Woodward 1964, Collé and Kishore1997). For example, when ^{222}Rn is measured by counting the emissions of its

[7] The negative bias of $\sqrt{N}$ is largely eliminated if one replaces it by $\sqrt{N+0.25}$. MARLAP recommends the estimator $\sqrt{N+1}$ although it is positively biased.

[8] 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.

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.

Both counting models may also be invalid if the total dead time of the measurement is significant (see Section 19.6.3.1).

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 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-square 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.

19.6.3 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 N (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 $N = n$ 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 r 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

$$u^2(r) = \frac{n}{t^2} + \frac{n^2}{t^4} u^2(t) \qquad (19.20)$$

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: A source is counted for $t = 100$ s, where t has standard uncertainty $u(t) = 0.1$ s, and $n = 961$ counts observed. When $u(t)$ is ignored, the combined standard uncertainty of the count rate r is $u_c(r) = \sqrt{n/t^2}$, or 0.31 cps. When $u(t)$ is included, the combined standard uncertainty is

$$u_c(r) = \sqrt{\frac{n}{t^2} + \frac{n^2}{t^4}u^2(t)} = \sqrt{\frac{961}{10^4} + \frac{961^2}{10^8}0.1^2} \approx 0.31 \text{ cps}$$

In this case, the difference between the two uncertainty estimates is negligible.

EXAMPLE: A source is counted for $t = 100$ s, where $u(t) = 1$ s, and $n = 10{,}609$ counts observed. When $u(t)$ is ignored, $u_c(r) = \sqrt{n/t^2} = 1.03$ cps. When $u(t)$ is included,

$$u_c(r) = \sqrt{\frac{n}{t^2} + \frac{n^2}{t^4}u^2(t)} = \sqrt{\frac{10{,}609}{10^4} + \frac{10{,}609^2}{10^8}1^2} \approx 1.48 \text{ cps}$$

In this example the difference between the two estimates is clearly significant.

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 19.20 may still be used.[9]

19.6.3.1 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

[9] 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 $\lambda = R$.

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 $1 - m\tau / t$. 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-square test described in Section 18B.2 of Attachment 18B can be used for this purpose.

19.6.3.2 A Confidence Interval for the Count Rate

When the Poisson counting model 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:[10]

$$R_{\text{lower}} = \chi^2_{(1-\gamma)/2}(2n) / 2t$$
$$R_{\text{upper}} = \chi^2_{(1+\gamma)/2}(2n + 2) / 2t \qquad (19.21)$$

Here γ is the desired *confidence coefficient*, or the minimum probability of coverage, and $\chi^2_p(n)$ denotes the p-quantile of the chi-square distribution with n degrees of freedom (see Table G.3 in Appendix G). If $n = 0$, the chi-square distribution $\chi^2(n)$ is degenerate. For our purposes $\chi^2_p(0)$ should be considered to be 0.

[10] The chi-square 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 19.21. The relationship is such that if X is chi-square with $2n$ degrees of freedom and Y is Poisson with mean μ, then $\Pr[X \le 2\mu] = \Pr[Y \ge n]$.

EXAMPLE: Suppose 10 counts are observed during a 600-second instrument background measurement. Then the 95% confidence limits for the background count rate are

$$R_{\text{lower}} = \frac{\chi^2_{0.025}(20)}{(2)(600)} = \frac{9.59078}{1200} = 0.00799 \text{ cps}$$

$$R_{\text{upper}} = \frac{\chi^2_{0.975}(22)}{(2)(600)} = \frac{36.7807}{1200} = 0.03065 \text{ cps}$$

EXAMPLE: Suppose 0 counts are observed during a 600-second measurement. Then the 95% confidence limits for the count rate are

$$R_{\text{lower}} = \frac{\chi^2_{0.025}(0)}{(2)(600)} = 0 \text{ cps}$$

$$R_{\text{upper}} = \frac{\chi^2_{0.975}(2)}{(2)(600)} = \frac{7.3778}{1200} = 0.00615 \text{ cps}$$

19.6.4 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, the 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 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 $\bar{x}$ 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 $s(\bar{x})$ 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 false.

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-square statistic may be used to detect and quantify non-Poisson background variance (Currie 1972; see also Section 18B.3 of Attachment 18B), but chi-square 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

$$\xi_B^2 = \frac{1}{n-1}\left[\sum_{i=1}^{n-1}\left(\frac{N_{i+1}}{t_{i+1}} - \frac{N_i}{t_i}\right)^2 - \frac{\sum_{i=1}^{n} N_i}{\sum_{i=1}^{n} t_i}\sum_{i=1}^{n-1}\left(\frac{1}{t_{i+1}} + \frac{1}{t_i}\right)\right] \qquad (19.22)$$

may be used to estimate the non-Poisson variance of a net count rate due to background even if the background is not stationary. 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 19C describes a method for choosing an appropriate coverage factor when only few counts are observed.

19.6.5 Counting Efficiency

The counting efficiency for a measurement of radioactivity 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 spectrometry, for example). In other cases a single measured value is used (e.g., alpha 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

Several sources with the same geometry are prepared and used to calibrate a radiation counter. One blank measurement is made. Each source is counted once to obtain an estimate of the count rate, the estimates are averaged, and the average is used to calculate the counting efficiency. The sources are long-lived and all source count times are equal. Let

- C = concentration of standard solution ($C = 1500$, $u(C) = 20$ Bq g^{-1})
- M = mean mass of solution added to each source (0.09980 g, added by a 0.1-mL pipet)
- n = number of sources (15)
- N_B = blank count (90)
- t_S = source count time (300 s)
- t_B = blank count time (6000 s)
- $N_{S,i}$ = gross count observed during the measurement of the i^{th} source
- R_i = gross count rate observed in the i^{th} source measurement
- $\overline{R}$ = arithmetic mean of the gross count rates, R_i
- ε = estimated counting efficiency

Then the following equations may be used to calculate the mean efficiency and its standard uncertainty:

$$R_i = \frac{N_{S,i}}{t_S}, \qquad i = 1,2,...,n$$

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

$$s^2(\overline{R}) = \frac{1}{n(n-1)}\sum_{i=1}^{n}(R_i - \overline{R})^2$$

$$\varepsilon = \frac{\overline{R} - N_B / t_B}{CM}$$

$$u(\varepsilon) = \sqrt{\frac{s^2(\overline{R}) + N_B / t_B^2}{C^2 M^2} + \varepsilon^2\left(\frac{u^2(C)}{C^2} + \frac{u^2(M)}{M^2}\right)}$$

The source-to-source variability of the mass M is not explicitly evaluated, because it is included in the observed variability of the count rates, R_i. So, the standard uncertainty $u(M)$ represents only the uncertainty of the mean mass added by the pipet. This uncertainty arises from uncertainty in the capacity of the pipet, the density of the solution, temperature effects, and the analyst's technique. Assume for this example that $u(M)$ is 0.00050 g (about 0.5%).

Note that the uncertainty of the blank count, N_B, is negligible in this example and could have been ignored. It was included only for completeness.

Assume the observed source counts, $N_{S,i}$, are as follows:

15,708	15,946	15,953	16,012	16,066
15,924	15,844	16,020	15,877	16,061
16,120	15,902	16,211	16,181	15,984

Then the observed gross count rates, R_i, are:

52.360	53.153	53.177	53.373	53.553
53.080	52.813	53.400	52.923	53.537
53.733	53.007	54.037	53.937	53.280

The average of the gross count rates is calculated as follows.

$$\overline{R} = \frac{1}{15}\sum_{i=1}^{15} R_i = \frac{799.363}{15} = 53.2909$$

The experimental variance of $\overline{R}$ is

$$s^2(\overline{R}) = \frac{1}{15(15-1)}\sum_{i=1}^{15}(R_i - 53.2909)^2 = 0.012876$$

Then the estimated counting efficiency is

$$\varepsilon = \frac{53.2909 - 90/6000}{(1500)(0.09980)} = 0.355884$$

and the standard uncertainty of ε is given by

$$u(\varepsilon) = \sqrt{\frac{0.012876 + 90/6000^2}{(1500)^2(0.09980)^2} + 0.355884^2\left(\frac{20^2}{1500^2} + \frac{0.0005^2}{0.09980^2}\right)} = 0.0051$$

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 a second component of uncertainty due to variations of the true efficiency during subsequent measurements. The second component may be written as $\varepsilon^2\varphi^2$, where φ is an estimate of the coefficient of variation of the true efficiency. Then the standard uncertainty of ε equals the square root of the sum of the squares of the two components.

In the example above, the experimental variance of the count rates, $s^2(R_i)$, might be used to estimate φ^2. Procedure E2, which is described in Section 18B.2 of Attachment 18B, is a step-by-step procedure for estimating such "excess" variance in a series of measurements. However, if the procedure were applied to the series of measurements made in the example, the estimated variance might be inflated by errors in the pipetting of the standard solution. The resulting estimate

would therefore tend to be an upper bound. A lower bound for the excess variance could be estimated by making replicate measurements of only one source, thus eliminating the effects of pipetting errors but also unfortunately eliminating the effects of variable source geometry. A better approach is to weigh the amount of standard solution added to each source, use the results, M_i, to calculate 15 individual estimates of the counting efficiency, ε_i, and estimate the excess variance of the values ε_i.

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 counting instruments. 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: Suppose the counting efficiency for a measurement is modeled by the equation $\varepsilon = A\exp(-BM_S)$, 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, or the variables ε and Y in the model may be replaced by the expressions $A\exp(-BM_S)$ and M_S / M_C, respectively.

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 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.

19.6.6 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 website (www.nndc.bnl.doe.gov).

19.6.7 Gamma Spectrometry

There are a number of sources of measurement uncertainty in gamma 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
- Dead time

See Chapter 17 for further discussion of measurement models and uncertainty analysis for gamma spectrometry.

19.6.8 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.

The uncertainty of the result of a balance measurement generally has components associated with balance calibration, linearity, repeatability, day-to-day 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 19G of this chapter describes several of these uncertainty components 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 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.

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 19G of this chapter, is to treat a_L as the amplitude of a sinusoidal function. 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 19G.

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}, and multiplying the difference, I_{Net}, by the buoyancy correction factor, B. That is,

$$m = I_{Net}B = (I_{Gross} - I_{Tare})B \tag{19.23}$$

The standard uncertainty of m is given by

$$u(m) = \sqrt{B^2\left(I_{Net}^2(\varphi_{Cal}^2 + \varphi_{Env}^2) + a_L^2 + 2s_r^2\right) + I_{Net}^2 u^2(B)} \tag{19.24}$$

where

- m is the buoyancy-corrected net mass
- I_{Net} is the net balance indication ($I_{Gross} - I_{Tare}$)
- I_{Tare} is the balance indication for the tare mass
- I_{Gross} is the balance indication for the gross mass
- B is the buoyancy correction factor

Attachment 19G describes uncertainty equations for use in other circumstances.

19.6.9 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 density of a liquid depends on its temperature. For this reason, when a volume is being measured, one should determine 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. One should also determine whether the effect of temperature is significant for the measurement. Often it is not, but in some cases a correction for thermal expansion may be necessary.

The standard uncertainty for a volumetric measurement includes components associated with the capacity of the measuring device, temperature effects, repeatability, and the analyst's bias in using the device (e.g., reading a meniscus).

The capacity of a volumetric pipet or flask (at 20°C) is generally specified with a tolerance a, which may be assumed to represent the half-width of a triangular distribution (e.g., see ASTM

1994 and ASTM 1995). Assuming a triangular distribution, one evaluates the uncertainty component of the volume associated with the capacity as $a/\sqrt{6}$.

The relative standard uncertainty due to temperature variations is typically a Type B standard uncertainty, which may be derived from a temperature range, $T \pm \delta T$, and the liquid's coefficient of thermal expansion, β, at the center of the range. Assuming a rectangular distribution for the temperature with half-width δT, the relative standard uncertainty component due to temperature variations is $|\beta|\delta T/\sqrt{3}$.

The nominal capacity of any volumetric glassware is usually specified at 20°C. If the glassware is used at a different temperature, the capacity is slightly different. Temperature effects on the capacity are generally very small (much smaller than the effects on the density of the liquid) and for this reason one may usually ignore them. The relationship between the capacity and the temperature is given approximately by

$$V_T = V_{20}(1 + \alpha(T - 20)) \tag{19.25}$$

where

T	is the temperature (°C)
V_T	is the capacity at temperature T
V_{20}	is the capacity at 20°C
α	is the glassware's coefficient of thermal cubical expansion ($°C^{-1}$)

The value of α for ASTM Type I, Class A, borosilicate glassware is approximately 0.00001 $°C^{-1}$; so, the capacity increases by only about 0.001% for each degree Celsius of temperature increase.

An analyst may calibrate a pipet 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 tolerance 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 procedure produces a set of balance indications, I_i, which are averaged to obtain the arithmetic mean $\bar{I}$. 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 divided by the density of the liquid at room temperature. A correction factor for thermal expansion of the pipet may also be included, if necessary.

$$v = \bar{I}Z \qquad \text{where} \qquad Z = \frac{1 - \rho_{A,C}/\rho_C}{\rho_M - \rho_{A,M}} \tag{19.26}$$

and where

ρ_M is the density of the liquid
$\rho_{A,M}$ 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
$\rho_{A,C}$ is the density of the air at the time of the balance calibration

The calibration is most often performed using water.

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 (ASTM 2000). Table 19.2, which is taken from ASTM E542, shows the density of air-free water at various temperatures. Attachment 19G of this chapter describes an equation to calculate the density of air as a function of temperature, pressure, and humidity.

TABLE 19.2 — Density of air-free water

Temperature, °C	Density, g/cm³	Temperature, °C	Density, g/cm³
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		

1447 The volume, v, estimated by the calibration may be substituted for the pipet's nominal capacity
1448 when the pipet is used later in an analytical measurement. The uncertainty of v as an estimate of
1449 the mean volume may be calculated as follows.

$$\begin{aligned} u(\bar{I}Z) &= \sqrt{Z^2 u^2(\bar{I}) + \bar{I}^2 u^2(Z)} \\ &= \sqrt{Z^2\left(s^2(\bar{I}) + \bar{I}^2(\varphi_{Cal}^2 + \varphi_{Env}^2)\right) + \bar{I}^2 u^2(Z)} \\ &= \sqrt{Z^2 \frac{s^2(I_j)}{n} + v^2\left(\varphi_{Cal}^2 + \varphi_{Env}^2 + \frac{\beta^2 \delta T^2}{3}\right)} \end{aligned} \tag{19.27}$$

1450 where φ_{Cal} and φ_{Env} denote the relative standard uncertainties of mass measurements associated
1451 with balance calibration and environmental factors, respectively (see Section 19.6.8). Note that
1452 the uncertainty of the buoyancy correction factor has been ignored here and the standard uncer-
1453 tainty of Z has been equated with the component due to thermal expansion of the liquid, which is
1454 assumed to be dominant. Also note that the correlation between Z and $\bar{I}$ induced by temperature
1455 effects on both the liquid density and the balance sensitivity is unknown and has been ignored.

1456 The uncertainty of v as a predictor of the true volume that will be dispensed during a subsequent
1457 measurement includes additional components for repeatability and temperature variability.

$$u(v) = \sqrt{Z^2 s^2(I_j)\left(1 + \frac{1}{n}\right) + v^2\left(\varphi_{Cal}^2 + \varphi_{Env}^2 + \frac{2\beta^2 \delta T^2}{3}\right)} \tag{19.28}$$

1458 Note that if a different analyst performs the measurement, there may be an additional uncertainty
1459 component associated with the difference in individual techniques.

1460 If the mean volume is within specified tolerances, a slightly simpler approach is possible. The
1461 pipet's nominal capacity may be used as the volume v and the tolerance a may be used in a Type
1462 B evaluation of standard uncertainty. In this case, the standard uncertainty of v is evaluated as
1463 shown below.

$$u(v) = \sqrt{\frac{a^2}{6} + Z^2 s^2(I_j) + \frac{v^2 \beta^2 \delta T^2}{3}} \tag{19.29}$$

The experimental procedure outlined above may also be adapted for other volume measuring devices, including flasks and graduated cylinders.

The manufacturers of certain types of automatic pipetting devices (e.g., Eppendorf® pipettors) provide specifications for bias and imprecision. For these devices the manufacturer's specifications for bias and imprecision may be assumed. In this case the Type B standard uncertainty of a pipetted volume v is

$$u(v) = \sqrt{\frac{a^2}{6} + s^2 + \frac{v^2 \beta^2 \delta T^2}{3}} \qquad (19.30)$$

where a is the manufacturer's stated bias tolerance, assumed to represent the half-width of a triangular distribution, and s is the stated standard deviation. This approach has the advantage of simplicity; however, since many analysts may not achieve the same accuracy as the manufacturer, the standard uncertainty given by Equation 19.30 may be unrealistic.

19.6.10 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:** The readability of a digital balance is 0.1 mg. Therefore, the minimum standard uncertainty of a measured mass is $0.1 / 2\sqrt{3} = 0.029$ mg.

EXAMPLE: A computer printout shows the result x of a measurement as

```
3.40E+01 +- 9.2E-02
```

where the expanded uncertainty is calculated using a coverage factor of 2. The measured value is rounded to the nearest multiple of 0.1. So, the standard uncertainty of x is

$$u(x) = \sqrt{\left(\frac{0.092}{2}\right)^2 + \left(\frac{0.1}{2\sqrt{3}}\right)^2} = 0.054.$$

19.6.11 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 which increases the combined standard uncertainty of the result. (Since its value is always 1, the factor F_S is an example of a "nominal value," as discussed in Section 19.5.5.) The uncertainty of F_S also increases the MDC and the MQC.

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 estimate the uncertainty, possibly with the aid of the information and methods presented in Appendix F. By default, if "hot particles" are not suspected, and if reasonable precautions are taken to homogenize (mix) the material and to obtain a sufficient number of particles in an unbiased subsample, one may simply assume a nominal relative standard uncertainty component of 5% for solid materials.

19.6.12 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 the measured concentration of a hypothetical laboratory sample with a specified concentration (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: Suppose the mathematical model for a radioactivity measurement is

$$X = \frac{N_S/t_S - N_B/t_B}{M_S Y \varepsilon e^{-\lambda(t_D + t_S/2)}}$$

where

X	is the activity concentration (Bq kg^{-1})
N_S	is the test source count
N_B	is the blank count
t_S	is the source count time (s)
t_B	is the blank count time (s)
t_D	is the decay time (s)
M_S	is the size of the test portion (kg)
Y	is the chemical yield
ε	is the counting efficiency
λ	is the decay constant (s^{-1})

With specified values for the concentration X, test portion size 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 $N_S = t_S(XM_SY\varepsilon \exp(-\lambda(t_D + t_S/2)) + N_B/t_B)$. 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 uncertainty propagation formula gives the combined variance of the output estimate X as

$$u_c^2(X) = \frac{u^2(N_S)/t_S^2 + u^2(N_B)/t_B^2}{M_S^2 Y^2 \varepsilon^2 e^{-2\lambda(t_D + t_S/2)}} + X^2\left(\frac{u^2(M_S)}{M_S^2} + \frac{u^2(Y)}{Y^2} + \frac{u^2(\varepsilon)}{\varepsilon^2}\right)$$

$$= \frac{(XM_SY\varepsilon e^{-\lambda(t_D + t_S/2)} + N_B/t_B)/t_S + N_B/t_B^2}{M_S^2 Y^2 \varepsilon^2 e^{-2\lambda(t_D + t_S/2)}} + X^2\left(\frac{u^2(M_S)}{M_S^2} + \frac{u^2(Y)}{Y^2} + \frac{u^2(\varepsilon)}{\varepsilon^2}\right)$$

19.7 Detection and Quantification Limits

19.7.1 Calculation of the Critical Value

In Section 19.4.1, 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

$$\Pr[\hat{S} > S_C \mid X = 0] = \alpha \tag{19.31}$$

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 19.31 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 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 radioanalysis, the following presentation focuses primarily on S_C. However, conversion of either of these values to the other is simple, because $y_C = S_C + \hat{B}$.

19.7.1.1 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

$$S_C = z_{1-\alpha}\sigma_0 \tag{19.32}$$

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 19D 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 19D.) Given σ_B, the standard deviation σ_0 of the net signal $\hat{S}$ under the null hypothesis is given equal to

$$\sigma_0 = \sigma_B\sqrt{1 + \frac{1}{n}} \tag{19.33}$$

19.7.1.2 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 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.

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,

$$\hat{Y} = N_S \qquad \hat{B} = \left(\frac{N_B}{t_B} + \hat{R}_I \right) t_S \tag{19.34}$$

and the net instrument signal is the *net count*, defined as

$$\hat{S} = N_S - \left(\frac{N_B}{t_B} + \hat{R}_I \right) t_S \tag{19.35}$$

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
- t_B is the count time for the blank

The net signal is always assumed to have zero mean.

THE POISSON-NORMAL APPROXIMATION

When Poisson counting statistics are assumed (possibly with additional variance components) and the instrument background remains stable at a level where the Poisson distribution is approximately normal, the critical net count is given approximately by the equation

$$S_C = z_{1-\alpha} t_S \sqrt{\frac{R_B + R_I}{t_S} + \frac{R_B}{t_B} + \xi_B^2 + \sigma^2(\hat{R}_I)} \tag{19.36}$$

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 (see Section 19.6.4), 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

$$S_C = z_{1-\alpha} \sqrt{R_B t_S \left(1 + \frac{t_S}{t_B}\right)} \tag{19.37}$$

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 19.37, 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.

$$S_C = z_{1-\alpha} \sqrt{\hat{R}_B t_S \left(1 + \frac{t_S}{t_B}\right)} \tag{19.38}$$

Equation 19.38 resembles Equation 19.37 (Currie's equation) 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 19D for other possible estimators.)

$$\hat{R}_B = \frac{N_B}{t_B} \tag{19.39}$$

The resulting formula, shown below, is equivalent to equations published by several authors (Currie 1968, Lochamy 1976, Strom and Stansbury 1992, ANSI 1996a).

$$S_C = z_{1-\alpha} \sqrt{N_B \frac{t_S}{t_B} \left(1 + \frac{t_S}{t_B}\right)} \tag{19.40}$$

If $\alpha = 0.05$ and $t_B = t_S$, Equation 19.40 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 19.40 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 19.40 produces type I errors more than 25% of the time regardless of the chosen significance level α. Attachment 19D describes several expressions for S_C that have been proposed for use in situations where the mean blank count is less than 100.

EXAMPLE

Problem: A 6000-s 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 $\alpha = 0.05$.

Solution:

$$S_C = z_{1-\alpha}\sqrt{N_B \frac{t_S}{t_B}\left(1 + \frac{t_S}{t_B}\right)}$$

$$= 1.645\sqrt{108\left(\frac{3000}{6000}\right)\left(1 + \frac{3000}{6000}\right)}$$

$$= 14.8 \text{ counts.}$$

EXAMPLE

Problem: Repeat the same problem assuming the blank correction, expressed as a count rate, has a non-Poisson uncertainty component of $\xi_B = 0.001$ cps (see Section 19.6.4).

Solution:

$$S_C = z_{1-\alpha}\sqrt{N_B \frac{t_S}{t_B}\left(1 + \frac{t_S}{t_B}\right) + \xi_B^2 t_S^2}$$

$$= 1.645\sqrt{108\left(\frac{3000}{6000}\right)\left(1 + \frac{3000}{6000}\right) + (0.001)^2(6000)^2}$$

$$= 15.6 \text{ counts.}$$

So, 15.6 may be a slightly more realistic value for the critical net count.

19.7.1.3 Reagent Blanks

Equation 19.40 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 reagent 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 instruments. If detection in a laboratory sample is defined relative to a reagent blank counted on a different instrument, Equation 19.40 is inappropriate. Even if a single instrument is used, the presence of positive amounts of analyte in the reagents probably invalidates the Poisson assumption. In principle, $\hat{B}$ should be estimated by converting the total analyte activity of the reagent blank Z_{RB} to an estimated gross count on the instrument used to measure the laboratory sample. Thus,

$$\hat{B} = F(Z_{RB}) \tag{19.41}$$

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

Z_{RB} is the estimated total activity of the reagent blank

Then the net count is $\hat{S} = \hat{Y} - \hat{B}$, whose critical value is

$$S_C = z_{1-\alpha}\sqrt{\sigma^2(\hat{Y}_0) + \sigma^2(\hat{B})} \tag{19.42}$$

where

$\sigma^2(\hat{Y}_0)$ is the variance of the gross count $\hat{Y}$ in the test source measurement when all of the analyte in the source is derived from reagents

$\sigma^2(\hat{B})$ 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 uncertainty 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.

19.7.2 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 probability $1 - \beta$ of obtaining a measured response greater than its critical value, leading one to conclude correctly that the analyte concentration is positive. 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

$$\Pr[\hat{S} \le S_C \mid X = x_D] = \beta \qquad (19.43)$$

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 19.43 in practice may be difficult. The 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. For purposes of regulatory compliance, an uncertainty interval or conservative upper bound for x_D may still be needed (see NRC 1984).

19.7.2.1 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,

$$\Pr[\hat{S} \le S_C \mid S = S_D] = \beta \tag{19.44}$$

where S denotes the true mean net signal.

19.7.2.2 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

$$S_C = z_{1-\alpha}\sigma_0 \tag{19.45}$$

as previously noted. Then, the minimum detectable net signal S_D is determined implicitly by the equation

$$S_D = S_C + z_{1-\beta}\sqrt{\sigma^2(\hat{S} \mid S = S_D)} \tag{19.46}$$

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 19.46 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 19.46 by algebraic manipulation into an explicit formula for S_D. For example, the variance of $\hat{S}$ often has the form

$$\sigma^2(\hat{S}) = aS^2 + bS + c \tag{19.47}$$

where S denotes the true mean net signal and the constants a, b, and c do not depend on S (see Section 19.7.2.3, "Poisson Counting"). In this case, the minimum detectable net signal is given approximately by

$$S_D = \frac{1}{I_\beta}\left(S_C + \frac{z_{1-\beta}^2 b}{2} + z_{1-\beta}\sqrt{bS_C + \frac{z_{1-\beta}^2 b^2}{4} + aS_C^2 + I_\beta c} \right) \tag{19.48}$$

where $I_\beta = 1 - z_{1-\beta}^2 a$.

If Equation 19.46 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.[11]

1. Set $S_D = S_C + z_{1-\beta}\sqrt{\sigma^2(\hat{S} \mid S = S_C)}$
2. **repeat**
3. Set $h = S_D$
4. Set $S_D = S_C + z_{1-\beta}\sqrt{\sigma^2(\hat{S} \mid S = S_D)}$
5. **until** $|S_D - h|$ is sufficiently small
6. **output** the solution S_D

In many cases, one iteration of the loop (Lines 2–5) provides an adequate approximation of S_D. In almost all cases, repeated iteration produces an increasing sequence of approximations

[11] 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 of the technique.

converging upward to the solution; so, the stopping condition at Line 5 may be replaced by "**until** $S_D \leq h$" to obtain full machine precision in the result.

19.7.2.3 Poisson Counting

If S_C is calculated using the Poisson model and the blank is measured with a sufficiently large number of counts, and if $\alpha = \beta$, the minimum detectable net signal S_D is given by the following simple equation.[12]

$$S_D = z^2_{1-\beta} + 2S_C \tag{19.49}$$

In the special case when $t_S = t_B$ and $\alpha = \beta = 0.05$, Equation 19.49 becomes

$$S_D = 2.71 + 2S_C \tag{19.50}$$

In the general case, S_D is determined from Equation 19.48 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

$$S_D = S_C + \frac{z^2_{1-\beta}}{2} + z_{1-\beta} \sqrt{\frac{z^2_{1-\beta}}{4} + S_C + R_B t_S \left(1 + \frac{t_S}{t_B} \right)} \tag{19.51}$$

As previously noted, counting data never follow the Poisson model exactly. Variable factors such as counting efficiency, and source geometry and placement tend to increase a, while interferences and background instability tend to increase c. For example, if the counting efficiency has a 2%

[12] 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 $\alpha = \beta$.

coefficient of variation and background instability contributes a non-Poisson standard deviation of 0.001 cps to the blank correction, then one might use Equation 19.48 with the values

$$a = (0.02)^2 \qquad b = 1 \qquad c = R_B t_S \left(1 + \frac{t_S}{t_B} \right) + (0.001)^2 t_S^2$$

19.7.2.4 The MDC

Traditionally the minimum detectable net signal S_D has been converted directly to the minimum detectable concentration x_D using the same measurement model used to convert an observed value of the signal $\hat{S}$ to a concentration $\hat{x}$. In a typical model, the net count is divided by the *sensitivity* A, which is the product of factors such as the count time, test portion size, counting efficiency, chemical yield, and decay factor. The sensitivity may also include the *subsampling factor*, denoted by F_S, which was defined in Section 19.6.11 as the ratio of the analyte concentration of a subsample to that of the original sample. This factor is always estimated to be 1 and is included only for its contribution to the measurement uncertainty.

If the sensitivity does not vary substantially from measurement to measurement, the MDC is given by

$$x_D = \frac{S_D}{A} \tag{19.52}$$

If the variance of A is not negligible, it increases the value of x_D. Recall that when the variance of the net count $\hat{S}$ has the form $\sigma^2(\hat{S}) = aS^2 + bS + c$, the minimum detectable net instrument signal may be approximated by Equation 19.48. If the sensitivity is normally distributed, the effect of its variance on the detection limit may be accounted for (approximately) by increasing the value of the constant a in Equation 19.48 by an amount equal to $\varphi_A^2(1 + a)$, where φ_A denotes the relative standard deviation of A.[13] For example, in the Poisson-counting scenario, where the value of a would otherwise be zero, a becomes φ_A^2. Then the MDC is given by

[13] The word "approximately" is used here because the signal is only approximately normal when its conditional distribution depends on the sensitivity in the manner described.

$$x_D = \frac{1}{AI_\beta}\left(S_C + \frac{z_{1-\beta}^2}{2} + z_{1-\beta}\sqrt{\frac{z_{1-\beta}^2}{4} + S_C + aS_C^2 + I_\beta R_B t_S\left(1 + \frac{t_S}{t_B}\right)}\right) \quad (19.53)$$

where $I_\beta = 1 - z_{1-\beta}^2 a$ and $a = \varphi_A^2$.

Often the distribution of A may not be well-known or may not be approximately normal. In this case, one may replace A in the formula by a somewhat low value, such as the β-quantile a_β of its distribution, and ignore its variance. Thus, assuming Poisson counting statistics, one may use Equation 19.53 with $a = 0$ and $A = a_\beta$. Alternatively, if the subsampling error is thought to be approximately normal, one may increase a by $\varphi_{Samp}^2(1 + a)$, where φ_{Samp}^2 denotes the relative subsampling variance, and ignore the subsampling error when estimating the quantile a_β (the approach used in Attachment 19E). If φ_{Samp}^2 is negligible, the MDC may be obtained directly from the minimum detectable net count S_D using the following formula.

$$x_D = \frac{S_D}{a_\beta} \quad (19.53)$$

When a "sample-specific" MDC is calculated, the measured value of the sensitivity $\hat{A}$ may be substituted for A in the equation for x_D and the variance of A may be ignored. Then, if the subsampling variance φ_{Samp}^2 is also negligible, the MDC is estimated by

$$x_D = \frac{S_D}{\hat{A}} \quad (19.54)$$

However, it should be remembered that the resulting value for the MDC has an uncertainty generated by the measurement uncertainties of the input estimates from which it is calculated. It may also be variable because of the variability of the true sensitivity factors (e.g., chemical yield).

19.7.2.5 Regulatory Requirements

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 ($\blacktriangle_B$) and the sensitivity ($\blacktriangle_A$). The critical net count S_C is increased by $\blacktriangle_B \hat{B}$, and the minimum detectable net count S_D is increased by $2\blacktriangle_B \hat{B}$.

The MDC is then calculated by dividing S_D by the sensitivity and multiplying the result by $1 + \Delta_A$. The approach of NUREG/CR-4007, which deals with detection limits, differs fundamentally from that of the *GUM*, which considers only measurement uncertainty. 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.

19.7.2.6 Testing 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

$$P = \sum_{j=k}^{n} \binom{n}{j} \beta^j (1-\beta)^{n-j} \quad \text{or} \quad 1 - \sum_{j=0}^{k-1} \binom{n}{j} \beta^j (1-\beta)^{n-j} \tag{19.55}$$

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).

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

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 2% 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 $P \leq 0.02$, reject the null hypothesis and conclude that the MDC was underestimated.

19.7.3 Calculation of the Minimum Quantifiable Concentration

The *minimum quantifiable concentration* (MQC), or the *minimum quantifiable value* of the concentration, was defined in Section 19.4.5 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 19.6.12 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

$$x_Q = k_Q \sqrt{\sigma^2(\hat{X} \mid X = x_Q)} \tag{19.56}$$

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 19.56 for x_Q using only algebraic manipulation. Otherwise, fixed-point iteration, which was introduced in Section 19.7.2, may be used. The use of fixed-point iteration for this purpose is shown below.

1. Set $x_Q = k_Q \sqrt{\sigma^2(\hat{X} \mid X = 0)}$
2. **repeat**
3. Set $h = x_Q$

4. Set $x_Q = k_Q\sqrt{\sigma^2(\hat{X} \mid X = x_Q)}$

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 $X = S / AF_S$, where S is the net count, A denotes the overall sensitivity of the measurement, and F_S is the subsampling factor, Equation 19.56 may be solved for x_Q to obtain the formula

$$x_Q = \frac{k_Q^2}{2AI_Q}\left(1 + \sqrt{1 + \frac{4I_Q}{k_Q^2}\left(R_B t_S\left(1 + \frac{t_S}{t_B}\right) + \xi_B^2 t_S^2 + R_I t_S + \sigma^2(\hat{R}_I)t_S^2\right)}\right) \qquad (19.57)$$

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, $\hat{A}$
φ_{Samp}^2 is the relative subsampling variance
I_Q is equal to $1 - k_Q^2(\varphi_{\hat{A}}^2 + \varphi_{\text{Samp}}^2)$

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 measurement error — it does not include the variance of the true sensitivity, A.

Note that Equation 19.57 defines the MQC only if $I_Q > 0$. If $I_Q \leq 0$, the MQC is defined to be 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

$$x_Q = \frac{k_Q^2}{2(1 - k_Q^2 a)}\left(b + \sqrt{b^2 + \frac{4c(1 - k_Q^2 a)}{k_Q^2}}\right) \tag{19.58}$$

For example, if pure Poisson counting statistics are assumed and there are no interferences, then $a = \varphi_A^2 + \varphi_{\text{Samp}}^2$, $b = 1 / A$, and $c = R_B t_S (1 + t_S / t_B) / A^2$.

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This section contains a combined list of references for Chapter 19 and its attachments.

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ATTACHMENT 19A
Distributions

19A.1 Introduction

This attachment 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-square, and exponential distributions. Poisson distributions in particular are important in radiation counting measurements and are described in Section 19.6.2.

19A.2 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.

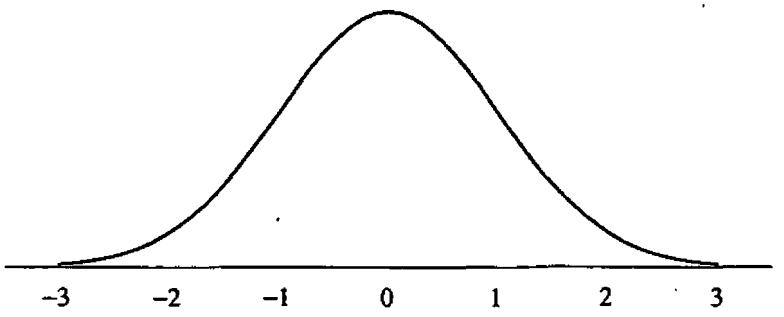

FIGURE 19.5 — A normal distribution

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.[14] 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-square, can be approximated by normal distributions under certain conditions.

The mean value of a normal distribution is also its mode, or most likely value, which corresponds to the location of the peak of the curve shown in Figure 19.5. Since the distribution is symmetric about this point, the mean is also the median, or the value that splits the range into equally likely portions.

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.3 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.

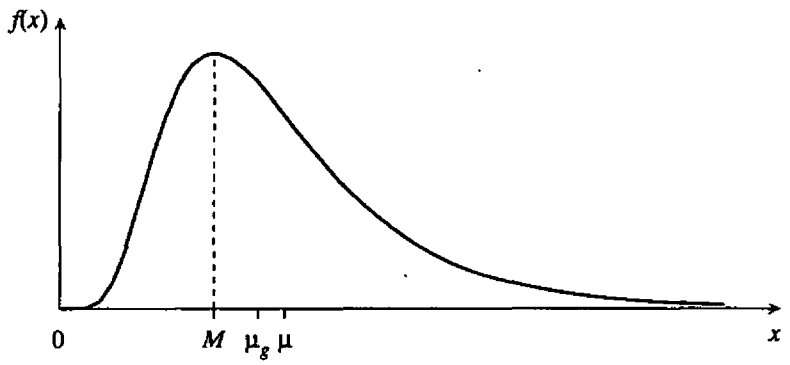

FIGURE 19.6 — A log-normal distribution

[14] The number of quantities required to obtain a sum that is approximately normal depends on the distribution of the quantities. If the distribution is already 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.

By definition, a quantity X has a log-normal 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 descriptors 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, median, and mode of a normal distribution are identical, for a log-normal distribution these three 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 and the mode M is smaller. The mean and mode may be calculated from the geometric mean and geometric standard deviation as shown in Table G.6 in Appendix G.[15]

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.4 Chi-square 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-square* (or *chi-squared*) *distribution with* ν *degrees of freedom*. A chi-square distribution, like a log-normal distribution, is asymmetric and does not include negative values. For large ν the chi-square distribution is approximately normal. Figure 19.7 shows the densities for chi-square distributions with 1, 2, 3, and 10 degrees of freedom.

[15] Given the mean μ and standard deviation σ, the geometric mean and geometric standard deviation may be calculated as $\mu_g = \mu^2 / \sqrt{\mu^2 + \sigma^2}$ and $\sigma_g = \exp\left(\sqrt{\ln(1 + \sigma^2 / \mu^2)}\right)$.

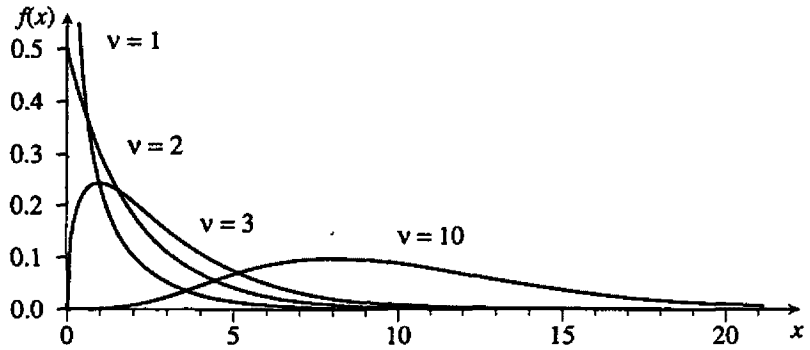

FIGURE 19.7 — Chi-square distributions

Chi-square distributions are used frequently in hypothesis testing, especially for tests of hypotheses about the variances of normally distributed data. Chi-square distributions also appear in least-squares analysis (see Attachment 19B).

A sum of independent chi-square random variables is also chi-square. Specifically, if X and Y are independent chi-square random variables with ν_1 and ν_2 degrees of freedom, respectively, then $X + Y$ has a chi-square distribution with $\nu_1 + \nu_2$ degrees of freedom.

The mean of a chi-square distribution equals the number of degrees of freedom ν, and the variance equals 2ν. The mode equals zero if $\nu \leq 2$ and equals $\nu - 2$ otherwise. The median does not have a simple formula.

19A.5 T-Distributions

If Z is standard normal, X is chi-square with ν degrees of freedom, and Z and X are independent, then $Z / \sqrt{X / \nu}$ has a *Student's t-distribution with* ν *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.

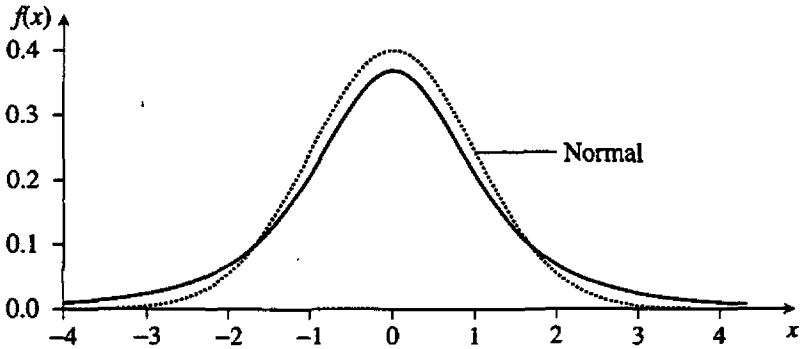

FIGURE 19.8 — The *t*-distribution with 3 degrees of freedom

When ν is large, the *t*-distribution is virtually identical to the standard normal distribution.

The median and mode of a *t*-distribution are both zero. The mean is also zero if $\nu > 1$ but is undefined for $\nu = 1$. The variance equals $\nu / (\nu - 2)$ if $\nu > 2$ 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 19C 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-square with ν degrees of freedom, Z and X are independent, and δ is a constant, then $(Z + \delta) / \sqrt{X / \nu}$ has the *non-central t-distribution* with ν degrees of freedom and non-centrality parameter δ. When the (central) *t*-distribution is used to test the null hypothesis that two normal distributions have the same mean, a non-central *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 non-central *t*-distribution with non-centrality parameter

$$\delta = \frac{\mu_Y - \mu_X}{\sigma\sqrt{1 + 1/n}}$$

if $\mu_X \neq \mu_Y$.

The non-central *t*-distribution is useful in the theory of detection limits and appears in Section 19D.3.2 of Attachment 19D.

19A.6 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).

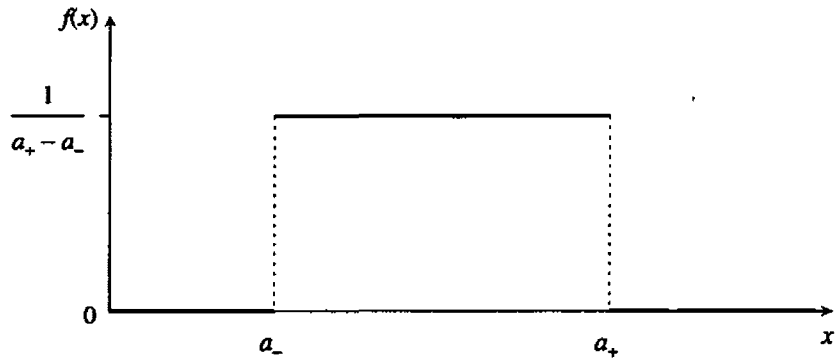

FIGURE 19.9 — A rectangular distribution

The mean and median of the rectangular distribution equal the midrange $(a_- + a_+) / 2$, and the standard deviation is $(a_+ - a_-) / 2\sqrt{3}$. The rectangular distribution is multimodal.

Rectangular distributions are frequently used for Type B evaluations of standard uncertainty (see Sections 19.5.2.2 and 19.6.10).

19A.7 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 19.5.2.2. 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.

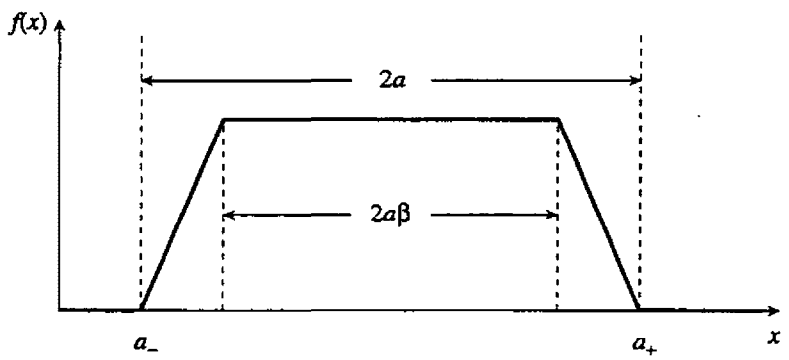

FIGURE 19.10 — A trapezoidal distribution

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 distribution*, 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.6.

19A.8 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 mode is zero, and the median is the same as the half-life of the radionuclide. The pdf for an exponential distribution is shown in Figure 19.11.

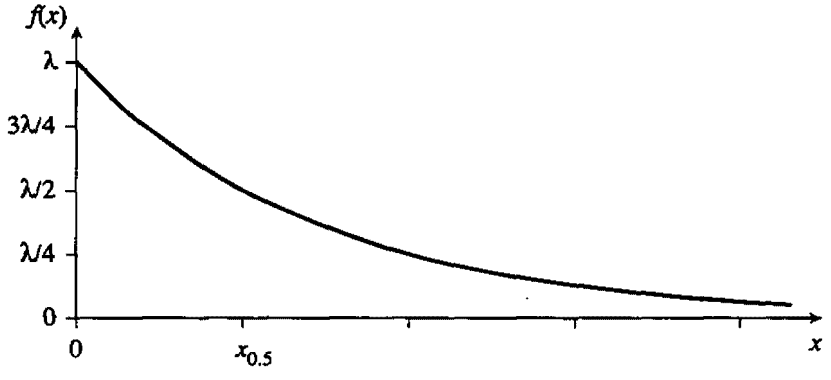

FIGURE 19.11 — An exponential distribution

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, the waiting times between counts are exponentially distributed with parameter R_B.

19A.9 Binomial Distributions

The *binomial distribution*, introduced in Section 19.6.2, 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 well approximated 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

$$\Pr[X=k]=\binom{n}{k} p^{k}(1-p)^{n-k} \tag{19.61}$$

19A.10 Poisson Distributions

As explained in Section 19.6.2, 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

$$\Pr[X = n] = e^{-\mu}\frac{\mu^{n}}{n!} \tag{19.62}$$

The Poisson distribution is related to the chi-square distribution, since

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

$$\Pr[X \le n] = \Pr[\chi^2(2n+2) \ge 2\mu] \quad \text{and} \quad \Pr[X \ge n] = \Pr[\chi^2(2n) \le 2\mu] \tag{19.63}$$

where $\chi^2(\nu)$ denotes a chi-square random variable with ν degrees of freedom. This fact allows one to use quantiles of a chi-square distribution to construct a confidence interval for μ based on a single observation $X = n$. Table 19.3 lists 95% two-sided confidence intervals for μ some small values of n. For larger 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):

$$\chi^2_p(\nu) \approx \nu\left(1 - \frac{2}{9\nu} + z_p\sqrt{\frac{2}{9\nu}}\right)^3 \tag{19.64}$$

As noted above, when the mean μ is large, the Poisson distribution may be approximated by a normal distribution. Specifically,

$$\Pr[X \le n] \approx \Phi\left(\frac{n + 0.5 - \mu}{\sqrt{\mu}}\right) \tag{19.65}$$

where Φ denotes the distribution function of the standard normal distribution. For most purposes, this approximation is adequate if $\mu \ge 20$.

19A.11 References

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ATTACHMENT 19B
Multicomponent Analyses

19B.1 Matrix Equations

A multicomponent mathematical model may require the simultaneous solution of a system of equations formulated in terms of vector and matrix operations, which are implemented in software. For example, one procedure for radiostrontium analysis involves the precipitation of strontium from a sample, followed by multiple beta measurements of the precipitate over a period of time. Both ^{89}Sr and ^{90}Sr are beta emitters, and ^{90}Sr decays to ^{90}Y, another beta emitter. The half-life of ^{90}Y is short enough (64 h) that significant ingrowth occurs over a period of several days, allowing the activities of ^{89}Sr and ^{90}Sr to be determined from the changing count rate.

The net beta count y_i for a measurement of duration t_i at time Δt_i after precipitation has an expected value given by

$$a_{i1}x_1 + a_{i2}x_2 = E(y_i) \tag{19.66}$$

where

x_1 is the ^{89}Sr activity in the precipitate
x_2 is the ^{90}Sr activity in the precipitate
a_{i1} is a function of t_i, Δt_i, and the ^{89}Sr counting efficiency and half-life
a_{i2} is a function of t_i, Δt_i, and the ^{90}Sr and ^{90}Y counting efficiencies and half-lives

If m measurements are performed, Equation 19.66 is repeated for each measurement, giving a system of m equations. After replacing $E(y_i)$ by the measured value y_i, one can rewrite the equations as approximations in the form

$$\begin{aligned} a_{11}x_1 &+ a_{12}x_2 \approx y_1 \\ a_{21}x_1 &+ a_{22}x_2 \approx y_2 \\ &\vdots \\ a_{m1}x_1 &+ a_{m2}x_2 \approx y_m \end{aligned} \tag{19.67}$$

or in matrix form as $\boldsymbol{A}\boldsymbol{x} \approx \boldsymbol{y}$. If $m \geq 2$, the system of equations can be solved simultaneously for x_1 and x_2. If there are exactly two measurements ($m = 2$), the system can be solved easily without matrix operations, but if additional measurements are made ($m > 2$), a least-squares solution,

which typically involves matrix algebra, is required. The use of matrix algebra can make uncertainty propagation more tedious.

19B.2 Random Vectors and Matrices

Uncertainty propagation in matrix equations is best described in terms of random vectors and random matrices. A useful exposition of matrix theory in this manual is impractical; so, some familiarity with the basic concepts must be assumed. These basic concepts will be extended to incorporate randomness.

A *random vector* is a vector whose components are random variables. Similarly, a *random matrix* is a matrix whose components are random variables.

Vectors are usually denoted by bold lower-case letters and matrices by bold upper-case letters. The i^{th} component of a vector $\boldsymbol{v}$ is denoted by v_i. The ij^{th} component of a matrix $\boldsymbol{A}$ is usually denoted by a_{ij}. The transpose of a matrix $\boldsymbol{A}$ will be denoted here by $\boldsymbol{A}'$. If $\boldsymbol{A}$ is square and invertible, the inverse is denoted by $\boldsymbol{A}^{-1}$. The length of a vector $\boldsymbol{v}$ is denoted by $\|\boldsymbol{v}\|$.

The *expected value* of a random vector $\boldsymbol{x}$ is defined as the vector $E(\boldsymbol{x})$ whose i^{th} component is $E(x_i)$. The expected value of a random matrix $\boldsymbol{Y}$ is similarly defined as the matrix $E(\boldsymbol{Y})$ whose ij^{th} component is $E(y_{ij})$. The *covariance matrix* of a column vector $\boldsymbol{x}$ and a column vector $\boldsymbol{y}$ is defined by

$$\mathrm{Cov}(\boldsymbol{x},\boldsymbol{y}) = E\left[(\boldsymbol{x} - E(\boldsymbol{x}))(\boldsymbol{y} - E(\boldsymbol{y}))'\right] \tag{19.68}$$

The *covariance matrix* of a random column vector $\boldsymbol{x}$ (or the *variance-covariance matrix*) is defined by

$$V(\boldsymbol{x}) = \mathrm{Cov}(\boldsymbol{x},\boldsymbol{x}) \tag{19.69}$$

The covariance matrix gets its name from the fact that the ij^{th} component of $\mathrm{Cov}(\boldsymbol{x},\boldsymbol{y})$ equals the covariance $\mathrm{Cov}(x_i,y_j)$.[16] When $\boldsymbol{x}$ and $\boldsymbol{y}$ are vectors of measured values, the estimated covariance matrices will be denoted here by $\boldsymbol{u}(\boldsymbol{x},\boldsymbol{y})$ and $\boldsymbol{u}^2(\boldsymbol{x})$.

[16] In the literature, one often sees the covariance matrix for $\boldsymbol{x}$ and $\boldsymbol{y}$ denoted by Σ_{xy} and the variance-covariance matrix for $\boldsymbol{x}$ denoted by Σ_x.

19B.3 Linear Least Squares

Assume $y_1, y_2, \ldots, y_m$ are independent, normally distributed measured results and $V(y_i) = \sigma_i^2$ for each i. Let $x_1, x_2, \ldots, x_n$ denote unknown quantities on which the y_i depend and whose values one needs to determine. Assume the means $E(y_i)$ are related to the quantities x_j by the following system of equations.

$$\begin{aligned} a_{11}x_1 + a_{12}x_2 + \cdots + a_{1n}x_n &= E(y_1) \\ a_{21}x_1 + a_{22}x_2 + \cdots + a_{2n}x_n &= E(y_2) \\ &\vdots \\ a_{m1}x_1 + a_{m2}x_2 + \cdots + a_{mn}x_n &= E(y_m) \end{aligned} \qquad (19.70)$$

For example the y_i might be measured beta counts of a sample and the x_j could represent the unknown activities of ^{89}Sr and ^{90}Sr in the sample at the time of collection.

The linear system 19.70 can be represented using matrix notation as

$$Ax = E(y) \qquad (19.71)$$

Typically $E(y)$ is unknown and must be replaced in Equation 19.71 by the measured vector y, but there may be no vector x for which Ax exactly equals y. So, it is necessary to find an approximate solution $\hat{x}$ such that $A\hat{x}$ is close to y in some sense. The components of the difference $A\hat{x} - y$ are called *residuals,* and when $A\hat{x}$ is close to y, the residuals should be small. If $\sigma_i = 1$ for all i, the method of *least squares* finds a vector $\hat{x}$ that minimizes the sum of the squares of the residuals SSRES = $\| A\hat{x} - y \|^2$. If $\sigma \neq 1$ for some i, then both sides of equation i should be divided by σ_i before applying the least-squares method. So, if W denotes the $m \times m$ diagonal matrix whose i^{th} diagonal element is $1 / \sigma_i^2$, then SSRES = $(A\hat{x} - y)'W(A\hat{x} - y)$. In practice, the standard deviations σ_i are usually replaced by the standard uncertainties $u(y_i)$.

A least-squares solution always exists. If rank $A < n$, there may be more than one solution, but this case only occurs if the measurement process is inadequate even in principle for determining the unknown quantities. So, in practice rank $A = n$. (The *rank* of A is the number of linearly

independent columns or rows.) Under this assumption the unique least-squares solution is given by Equation 19.72.[17]

$$\hat{x} = (A^T W A)^{-1} A^T W y \tag{19.72}$$

When quantities such as the test portion size V and chemical yield Y can be factored out of the matrix A, it is generally better to do so. The presence of such variables increases the variance of the least-squares solution $\hat{x}$, making critical values unnecessarily large when they are calculated as described in Section 19B.6. When quantities such as V and Y are factored out, the components of the least-squares solution $\hat{x}$ must be divided by the missing factors to obtain activity concentrations, and the uncertainties in the factors must be propagated.

Approximating the standard deviations σ_i in the weight matrix W by the standard uncertainties $u(y_i)$ may bias the least-squares solution slightly if y_i and $u(y_i)$ are correlated, which happens, for example, when y_i is a measured count and $u(y_i)$ is the Poisson counting uncertainty calculated from a single measurement. This bias can be virtually eliminated by using the initial least-squares solution to refine the values of the standard uncertainties and then repeating the least-squares procedure using the refined estimates.

The solution $\hat{x}$ is a random vector, because it is a function of the random vector y. The covariance matrix for $\hat{x}$ is

$$\mathbf{u}^2(\hat{x}) = (A^T W A)^{-1} \tag{19.73}$$

The diagonal elements of this matrix are the variances of the components of $\hat{x}$, and the off-diagonal elements are the covariances. This expression for the covariance matrix is complete only when there are no uncertainties in the coefficient matrix A. A more general formula for the covariance matrix is presented in Section 19B.5.

In some cases, the variance of each y_i may be unknown, although all components of y are believed to have the same variance. When this is true, the solution $\hat{x}$ may be computed by

$$\hat{x} = (A^T A)^{-1} A^T y \tag{19.74}$$

[17] For some least-squares problems, a direct calculation of the solution $\hat{x}$ using Equation 19.72 can be computationally unstable. *Singular value decomposition* of the matrix A gives a more stable method for obtaining $\hat{x}$ but is beyond the scope of this document. The SVD method also allows one to find a least-squares solution (not unique) when rank $A < n$. See Lawson 1974 or Press et al. 1992 for more details.

2247 and the variance of the components y_i may be estimated by

$$u^2(y_i) = \frac{\|A\hat{x} - y\|^2}{m - n} \tag{19.75}$$

2248 (The use of Equation 19.75 is a Type A evaluation of uncertainty with $m - n$ degrees of
2249 freedom.) When this equation is used, the covariance matrix for $\hat{x}$ is

$$\mathbf{u}^2(\hat{x}) = u^2(y_i)(A'A)^{-1} \tag{19.76}$$

2250 **19B.4 General Least Squares**

2251 The general least-squares problem arises when there is a set of measured values $y_1, y_2, \ldots, y_m$,
2252 whose expected values are functions of an n-dimensional vector x of unknown quantities, as
2253 indicated by the following system of equations.

$$\begin{aligned} f_1(x) &= E(y_1) \\ f_2(x) &= E(y_2) \\ &\vdots \\ f_m(x) &= E(y_m) \end{aligned} \tag{19.77}$$

2254 The system of equations can be written in matrix form as $f(x) = E(y)$ The method of least squares
2255 finds a vector $\hat{x}$ that minimizes the sum of the squares of the residuals

$$\text{SSRES} = \sum_{i=1}^{m} \left(\frac{f_i(\hat{x}) - y_i}{u(y_i)} \right)^2 = (f(\hat{x}) - y)'W(f(\hat{x}) - y) \tag{19.78}$$

2256 When $f(\hat{x})$ can be written as $A\hat{x}$ for some matrix A, the problem is linear least squares, whose
2257 solution was presented in the preceding section. When the functions f_i are nonlinear but differen-
2258 tiable, the solution can be obtained by iterative approximation methods. The most commonly
2259 used algorithm for nonlinear least squares is the Levenberg-Marquardt algorithm (Press et al.
2260 1992). Whatever algorithm is used, it should compute the covariance matrix $u^2(\hat{x})$, described in
2261 the next section. For more details on nonlinear least-squares problems, see Marquardt 1963,
2262 Press et al. 1992, or Bevington 1992.

19B.5 The Covariance Matrix for a Least-Squares Solution

Let $A = \partial f / \partial x$ denote the $m \times n$ matrix whose ij^{th} component is $\partial f_i / \partial x_j$.[18] Then the covariance matrix for the least-squares solution $\hat{x}$ is approximately equal to $(A'WA)^{-1}$.

It often happens that the function f depends on variables other than x, whose values, like the components of y, are measured before the least-squares method is applied. In the strontium analysis described at the beginning of this attachment, the measured counting efficiencies for ^{89}Sr, ^{90}Sr, and ^{90}Y are good examples. Measurement uncertainties in these variables contribute to the uncertainties in the solution $\hat{x}$, although the least-squares covariance matrix $(A'WA)^{-1}$ accounts only for uncertainties in the measurement of y. Better estimates of the variances and covariances of the components of $\hat{x}$ require that the expression for the covariance matrix be expanded.

Let the additional measured quantities be written as a vector z with components $z_1, z_2, \ldots, z_r$, and write $f(x;z)$ to indicate that f depends on both x and z. Assume the components of z are measured independently of y, and the covariance matrix $u^2(z)$ is known. If the method of least squares is applied to find the unique solution $\hat{x}$ that minimizes SSRES, and if the uncertainties in the components z_i are small, the covariance matrix for the solution is

$$\mathbf{u}^2(\hat{x}) = (A'WA)^{-1} + \left(\frac{\partial \hat{x}}{\partial z}\right) \mathbf{u}^2(z) \left(\frac{\partial \hat{x}}{\partial z}\right)' \tag{19.79}$$

where $\partial \hat{x} / \partial z$ denotes the $n \times r$ matrix whose ij^{th} component is $\partial \hat{x}_i / \partial z_j$. The j^{th} column of $\partial \hat{x} / \partial z$ may be calculated using the formula

$$\frac{\partial \hat{x}}{\partial z_j} = (A'WA)^{-1} \left(\frac{\partial A'}{\partial z_j} W\left(y - f(\hat{x};z)\right) - A'W \frac{\partial f}{\partial z_j} \right) \tag{19.80}$$

If the uncertainties in the components z_i are not small, another method of solution may be needed (e.g., see Fuller 1987).

When the least-squares problem is linear, the j^{th} column of $\partial f / \partial z$ is given by the formula

[18] The matrix A is the *Jacobian* matrix of the component functions $f_1, f_2, \ldots, f_m$.

$$\frac{\partial \boldsymbol{f}}{\partial z_j} = \frac{\partial \boldsymbol{A}}{\partial z_j}\hat{\boldsymbol{x}} \tag{19.81}$$

2284 and the ij^{th} component is given by

$$\frac{\partial f_i}{\partial z_j} = \sum_{k=1}^{n} \frac{\partial a_{ik}}{\partial z_j}\hat{x}_k \tag{19.82}$$

2285 When the problem is nonlinear, the components $\partial f_i / \partial z_j$ are calculated by other means.

2286 **19B.6 Critical Values**

2287 The general approach to the determination of critical values even in the case of nonlinear least
2288 squares is conceptually no different from that outlined in Section 19.7.1. The standard uncer-
2289 tainty of a signal or response variable is determined under the null hypothesis H_0 and then multi-
2290 plied by an appropriate factor, such as the normal quantile $z_{1-\alpha}$. The response variable for a
2291 component x_j may be taken to be the corresponding component $\hat{x}_j$ of the least-squares solution
2292 vector. Let $\boldsymbol{x}^*$ denote the value of the vector $\boldsymbol{x}$ under H_0. It will be assumed here that $x_j^* = 0$, but
2293 note that the null hypothesis must give values not only to x_j but to all the components of $\boldsymbol{x}$,
2294 because the value of one component generally affects the measurement uncertainties of the other
2295 components of the solution vector. Generally, for this purpose one must use the measured values
2296 of all the components of $\boldsymbol{x}$ except x_j, although these values may not be known accurately.

2297 To determine the critical value, first calculate the vector $\boldsymbol{y}^* = \boldsymbol{f}(\boldsymbol{x}^*)$, which is the expected value of
2298 $\boldsymbol{y}$ under H_0. If the least-squares problem is linear, then $\boldsymbol{y}^* = \boldsymbol{A}\boldsymbol{x}^*$. Next calculate the diagonal
2299 weight matrix $\boldsymbol{W}$, whose i^{th} diagonal element is the inverse $1 / u^2(y_i)$ of the estimated variance of
2300 y_i under the null hypothesis. For example, if the problem is the strontium problem described in
2301 Section 19B.1, in which y_i denotes a net count, then $u^2(y_i)$ might be the counting variance given
2302 by

$$u^2(y_i) = a_{i1}x_1^* + a_{i2}x_2^* + R_{B,i}t_i\left(1 + \frac{t_i}{t_{B,i}}\right) \tag{19.83}$$

2303 where $R_{B,i}$ is the blank count rate and $t_{B,i}$ is the corresponding count time. Finally, evaluate the
2304 covariance matrix $\boldsymbol{C}$ for the solution of the least-squares problem $\boldsymbol{f}(\hat{\boldsymbol{x}}) \approx \boldsymbol{y}^*$, as described in

Section 19B.5. (The solution vector $\hat{x}$ here equals x^* because of the method by which y^* was constructed.) Then the critical value of the j^{th} component $\hat{x}_j$ is $z_{1-\alpha}\sqrt{c_{jj}}$, where $z_{1-\alpha}$ is the $(1 - \alpha)$-quantile of the standard normal distribution.

19B.7 Detection and Quantification Limits

Computing the minimum detectable value of a component x_j requires one to find the value d such that $d = z_{1-\alpha}\sqrt{V(0)} + z_{1-\beta}\sqrt{V(d)}$, where $V(x_j)$ denotes the variance of the estimator $\hat{x}_j$ as a function of the true value x_j. The value of $V(x_j)$ is the j^{th} diagonal element of the covariance matrix $\boldsymbol{C}$ determined under the assumption that the true value of the j^{th} component is x_j. Solving for d precisely generally requires an iterative algorithm, which generates a sequence of values converging to d. Given that $V(x_j)$ and its derivative can be calculated, the equation may be solved by Newton-Raphson iteration. A simpler version of fixed-point iteration, which does not involve the derivative, may also be used. The use of fixed-point iteration for this purpose is described in Section 19.7.

The problem of determining the minimum quantifiable value of a concentration estimated by the least-squares methods is similar to that of finding the minimum detectable value and generally requires an iterative algorithm (e.g., see Section 19.7).

19B.8 References

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ATTACHMENT 19C
Estimation of Coverage Factors

19C.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 19C.3 applies the method to Poisson counting uncertainties.

19C.2 Procedure

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 distribution 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.

First compute the *effective degrees of freedom* ν_{eff} of the measurement using the *Welch-Satterthwaite* formula

$$\nu_{\text{eff}} = \frac{u_c^4(y)}{\sum_{i=1}^{N} \frac{u_i^4(y)}{\nu_i}} \tag{19.84}$$

Here $u_i(y) = |\partial y / \partial x_i|\, u(x_i)$ 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 is defined to be

$$\nu_i = \frac{1}{2} \frac{u^2(x_i)}{\sigma^2[u(x_i)]} = \frac{1}{2} \left(\frac{\Delta u(x_i)}{u(x_i)} \right)^{-2} \tag{19.85}$$

where $\Delta u(x_i)$ is the estimated standard deviation of the standard uncertainty $u(x_i)$. Estimation of $\Delta u(x_i)$ often requires professional judgment.

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 19.6.10). 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.

The coverage factor k_p is defined to be the $(1 + p) / 2$-quantile $t_{(1+p)/2}(\nu_{eff})$ of a t-distribution with ν_{eff} degrees of freedom.[19] 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 $n < \nu_{eff} < n + 1$, then use either $k_p = t_{(1+p)/2}(\nu_{eff})$ or

$$k_p = (n + 1 - \nu_{eff})\, t_{(1+p)/2}(n) + (\nu_{eff} - n)\, t_{(1+p)/2}(n + 1) \qquad (19.86)$$

The expanded uncertainty $U_p = k_p u_c(y)$ is estimated to have a coverage probability approximately equal to p.

19C.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 ν for the evaluation should be determined from $\Delta u(n)$. The standard deviation of $\sqrt{n}$ is always less than 0.65.[20] If n is greater than about 10, the standard deviation of $\sqrt{n}$ is

[19] 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.

[20] 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 $f(\lambda)$ whose value is the variance of the square root of a Poisson random variable with mean λ. The first derivative of f is positive, decreasing, and convex between $\lambda = 0$ and the location of the maximum of the function at $\lambda = 1.31895$; so, Newton's Method converges to the solution from below. The maximum value of f is found to be $(0.642256)^2$.

approximately equal to 0.5, and, in this case, Equation 19.85 gives the estimate $\nu \approx 2n$. For smaller values of n, the same approximation is inadequate.

MARLAP recommends that the standard uncertainty $u(n)$ and degrees of freedom ν for a Poisson measured value n be estimated by

$$u(n) = \sqrt{n} \qquad \text{and} \qquad \nu = 2n \tag{19.87}$$

or, if very low counts are possible, by

$$u(n) = \sqrt{n+1} \qquad \text{and} \qquad \nu = 2(n+1) \tag{19.88}$$

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 ν in Equation 19.88 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 ν tend to give conservative results.

19C.4 References

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ATTACHMENT 19D
Low-Background Detection Limits

19D.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.

19D.2 Calculation of the Critical Value

The critical value of the net signal S_C was defined earlier by the relation

$$\Pr[\hat{S} > S_C \mid X = 0] = \alpha \tag{19.89}$$

When the signal assumes only discrete values (e.g., numbers of counts), there may be no value S_C that satisfies Equation 19.89 exactly. The critical value in this case is defined as the smallest value S_C such that $\Pr[\hat{S} > S_C \mid X = 0] \leq \alpha$.

19D.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

$$S_C = z_{1-\alpha}\sigma_0 \tag{19.90}$$

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 ν degrees of freedom, the multiplier $z_{1-\alpha}$ should be replaced by $t_{1-\alpha}(\nu)$, the $(1 - \alpha)$-quantile of the t-distribution with ν degrees of freedom (cf. Type A evaluation of standard uncertainty in Section 19.5.2.1). Thus,

$$S_C = t_{1-\alpha}(\nu)\,\hat{\sigma}_0 \tag{19.91}$$

Table G.2 in Appendix G lists values of $t_{1-\alpha}(\nu)$. In general, $t_{1-\alpha}(\nu)$ is greater than $z_{1-\alpha}$, but the two values are approximately equal if ν 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,

$$\hat{\sigma}_0 = s_B\sqrt{1 + \frac{1}{n}} \tag{19.92}$$

The number of degrees of freedom, ν, in this case equals $n - 1$; so, the critical value of $\hat{S}$ is

$$S_C = t_{1-\alpha}(n-1)\, s_B\sqrt{1 + \frac{1}{n}} \tag{19.93}$$

19D.2.2 Poisson Counting

It is assumed here, as in Section 19.7, that the instrument is a radiation counter and the instrument signal is the gross count. Therefore,

$$\hat{Y} = N_S \qquad \hat{B} = \left(\frac{N_B}{t_B} + \hat{R}_I\right) t_S \tag{19.94}$$

and the net instrument signal is the *net count*, defined as

$$\hat{S} = N_S - \left(\frac{N_B}{t_B} + \hat{R}_I\right) t_S \tag{19.95}$$

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
t_B	is the count time for the blank

2434 If the mean blank count rate, R_B, is well-known and there are no interferences, then according to
2435 the Poisson model, the critical gross count, y_C, equals the smallest nonnegative integer n such that

$$e^{-R_B t_S} \sum_{k=0}^{n} \frac{(R_B t_S)^k}{k!} \geq 1 - \alpha \tag{19.96}$$

2436 Then S_C, the critical net count, equals $y_C - N_B t_S / t_B$. Table 19.4 shows critical gross counts for
2437 $\alpha = 0.05$ for small values of $R_B t_S$ (adapted from NRC 1984).[21] To use the table, one calculates the
2438 value of $R_B t_S$, finds the appropriate line in the table, and compares the observed gross count N_S to
2439 the value of y_C read from the table. The analyte is considered detected if and only if $N_S > y_C$.
2440 When $R_B t_S$ is greater than about 20, y_C may be approximated by

$$y_C = \lfloor 0.5 + R_B t_S + z_{1-\alpha}\sqrt{R_B t_S} \rfloor \tag{19.97}$$

2441 where $z_{1-\alpha}$ denotes the $(1 - \alpha)$-quantile of the standard normal distribution, and $\lfloor x \rfloor$ denotes the
2442 largest integer not greater than x.

TABLE 19.4 — 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

[21] The breaks in the table occur at $R_B t_S = 0.5\ \chi^2_{0.05}(2y_C)$ and $0.5\ \chi^2_{0.05}(2y_C + 2)$.

When the blank count rate R_B is low, which is often true for alpha counting, measuring its value with good relative precision tends to be difficult, especially if the instrument background tends to drift. However, a conservative bound, such as a 1 - α upper confidence limit, may be used if one wishes to limit type I error rates and is willing to tolerate the resulting higher detection limits. More commonly used methods for calculating the critical value are described below.

THE POISSON-NORMAL APPROXIMATION

As stated in Section 19.7.1.2, 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

$$S_C = z_{1-\alpha} t_S \sqrt{\frac{R_B + R_I}{t_S} + \frac{R_B}{t_B} + \xi_B^2 + \sigma^2(\hat{R}_I)} \tag{19.98}$$

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

$$S_C = z_{1-\alpha} \sqrt{R_B t_S \left(1 + \frac{t_S}{t_B}\right)} \tag{19.99}$$

Low mean blank levels cause the Poisson distribution to deviate from the normal model. Figure 19.12 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.[22]

---

[22] 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

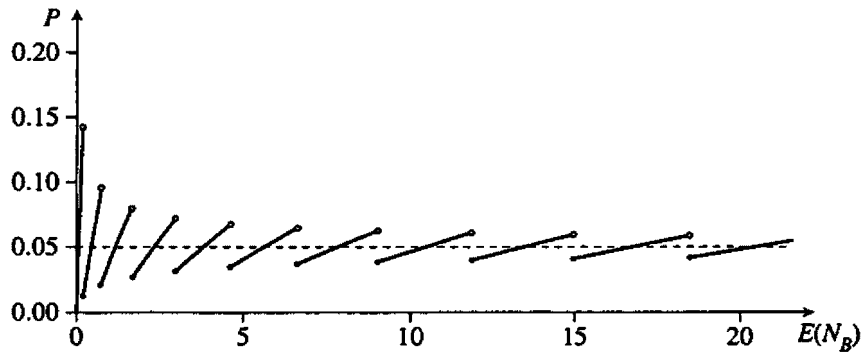

FIGURE 19.12 — Type I error rate for the Poisson-normal approximation ($t_B = t_S$)

In Equation 19.99, R_B denotes the *true* mean blank count rate, which can only be estimated. In practice, one must substitute an estimated value, $\hat{R}_B$, as shown in the following equation.

$$S_C = z_{1-\alpha}\sqrt{\hat{R}_B t_S\left(1 + \frac{t_S}{t_B}\right)} \tag{19.100}$$

The most frequently used expressions for S_C may be derived from Equation 19.100 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

$$\hat{R}_B = w_S\frac{N_S}{t_S} + w_B\frac{N_B}{t_B} \tag{19.101}$$

Brodsky 1992. The discontinuities occur at $\mu = k^2 / 2.33^2$ for $k = 1, 2, 3, \ldots$.

This estimate $\hat{R}_B$ 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.)[23]

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 $\hat{Y}$).

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 19.100 produces the following formula for an alternative critical value S_C.[24]

$$S_C = \frac{z_{1-\alpha}^2 w_S}{2}\left(1 + \frac{t_S}{t_B}\right) + z_{1-\alpha}\sqrt{\frac{z_{1-\alpha}^2 w_S^2}{4}\left(1 + \frac{t_S}{t_B}\right)^2 + N_B \frac{t_S}{t_B}\left(1 + \frac{t_S}{t_B}\right)} \qquad (19.102)$$

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 19.98), although at very low background 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).

[23] 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.

[24] 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.

$$S_C = z_{1-\alpha}\sqrt{N_B \frac{t_S}{t_B}\left(1 + \frac{t_S}{t_B}\right)} \qquad (19.103)$$

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 the standard approximation 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 19.7.1.2, 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 19.13 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 $\alpha = 0.05$.[25]

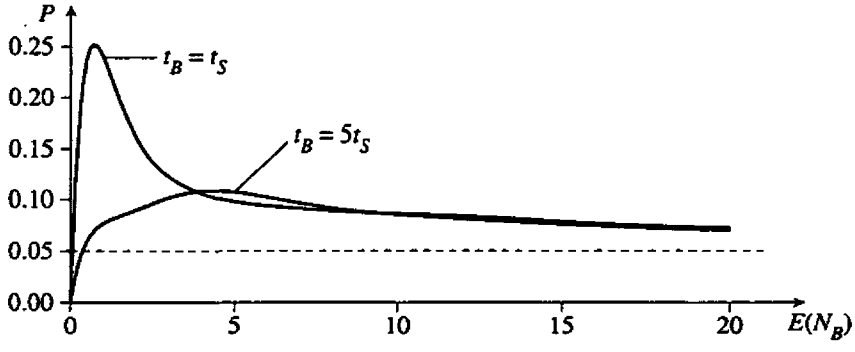

FIGURE 19.13 — Type I error rates for Formula A

[25] Probabilities on the two curves are calculated using the equation

$$P(\mu) = 1 - e^{-\mu(1+t_S/t_B)} \sum_{n=0}^{\infty} \frac{\mu^n}{n!} \sum_{k=0}^{\lfloor y_C(n) \rfloor} \frac{(\mu t_S / t_B)^k}{k!}$$

where $y_C(n) = n(t_S / t_B) + 1.645\sqrt{n(t_S / t_B)(1 + t_S / t_B)}$ and μ denotes the mean blank count. The same equation with different expressions for $y_C(n)$ is used to calculate the type I error rates shown in Figures 19.14–17.

FORMULA B

Another published formula for the critical value is (equivalent to) the following (Nicholson 1966).

$$\tilde{S}_C = z_{1-\alpha}\sqrt{N_S + N_B\frac{t_S^2}{t_B^2}} \tag{19.104}$$

The critical value calculated by Equation 19.104 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 19.100 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 19.104, one obtains Formula B (below), which is equivalent to the equation for the critical value given in *Atoms, Radiation, and Radiation Protection* (Turner 1995).

$$S_C = \frac{z_{1-\alpha}^2}{2} + z_{1-\alpha}\sqrt{\frac{z_{1-\alpha}^2}{4} + N_B\frac{t_S}{t_B}\left(1 + \frac{t_S}{t_B}\right)} \tag{19.105}$$

Formula B

Type I error rates for Formula B are shown in Figure 19.14.

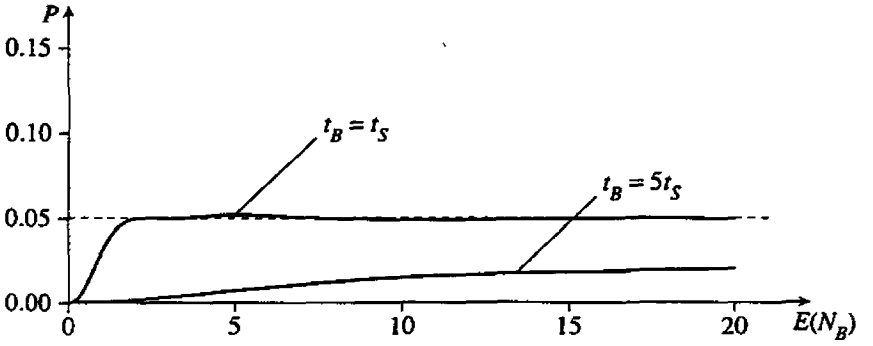

FIGURE 19.14 — Type I error rates for Formula B

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).[26]

$$\tilde{S}_C = z_{1-\alpha}\sqrt{(N_S + N_B)\frac{t_S}{t_B}} \tag{19.106}$$

Elimination of N_S from Equation 19.106 produces Formula C, shown below.

$$S_C = \frac{z_{1-\alpha}^2 t_S}{2t_B} + z_{1-\alpha}\sqrt{\frac{z_{1-\alpha}^2 t_S^2}{4t_B^2} + N_B\frac{t_S}{t_B}\left(1 + \frac{t_S}{t_B}\right)} \tag{19.107}$$

Formula C

Formula C is equivalent to the equation for the "decision threshold" given in Table 1 of ISO 11929-1 (ISO 2000a) for the case of fixed-time counting. Figure 19.15 shows type I error rates for Formula C.

[26] 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.

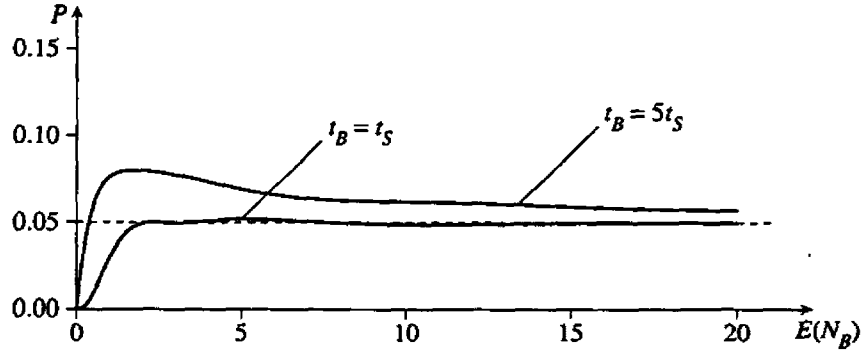

FIGURE 19.15 — Type I error rates for Formula C

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 2000b 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

$$Z = 2\left(\sqrt{\frac{N_S + d}{t_S}} - \sqrt{\frac{N_B + d}{t_B}}\right) \Big/ \sqrt{\frac{1}{t_S} + \frac{1}{t_B}} \qquad (19.108)$$

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). 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.

$$S_C = d\left(\frac{t_S}{t_B} - 1\right) + \frac{z_{1-\alpha}^2}{4}\left(1 + \frac{t_S}{t_B}\right) + z_{1-\alpha}\sqrt{(N_B + d)\frac{t_S}{t_B}\left(1 + \frac{t_S}{t_B}\right)} \qquad (19.109)$$

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

$$S_C = 1.35 + 2.33\sqrt{N_B + 0.4} \qquad (19.110)$$

Figure 19.16 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 $t_B \neq t_S$.

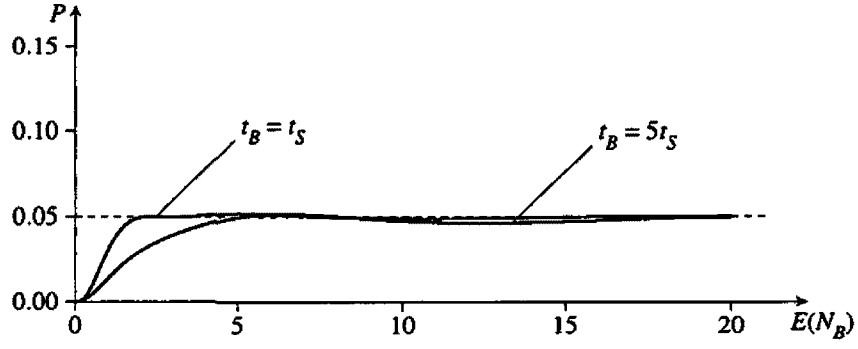

FIGURE 19.16 — Type I error rates for the Stapleton approximation

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 19.109 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.[27]

$$\sum_{k=N_S}^{N_S+N_B} \binom{N_S+N_B}{k} \left(\frac{t_S}{t_S+t_B}\right)^k \left(\frac{t_B}{t_S+t_B}\right)^{N_S+N_B-k} \le \alpha \qquad (19.111)$$

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[28]

$$\sum_{k=0}^{n} \binom{N_S+N_B}{k} \left(\frac{t_S}{t_S+t_B}\right)^k \left(\frac{t_B}{t_S+t_B}\right)^{N_S+N_B-k} \ge 1-\alpha \qquad (19.112)$$

The same (nonrandomized) test is implemented by calculating a critical gross count y_C equal to the smallest nonnegative integer n such that

$$\sum_{k=0}^{n} \binom{N_B+k}{N_B} \left(\frac{t_S}{t_S+t_B}\right)^k \ge (1-\alpha)\left(\frac{t_S+t_B}{t_B}\right)^{N_B+1} \qquad (19.113)$$

---

[27] The left-hand side of the inequality is a cumulative binomial probability (see Attachment 19A). 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).

[28] 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 − α 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*.

2552 Then the critical net count S_C equals $y_C - N_B(t_S / t_B)$. (Note that Inequality 19.113 is intended for
2553 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
2554 for integral values of the count time ratio t_B / t_S ranging from 1 to 5.

2555 Figure 19.17 shows the type I error rates for the nonrandomized exact test. (The type I error rate
2556 for the randomized version of the test equals 0.05 everywhere.)

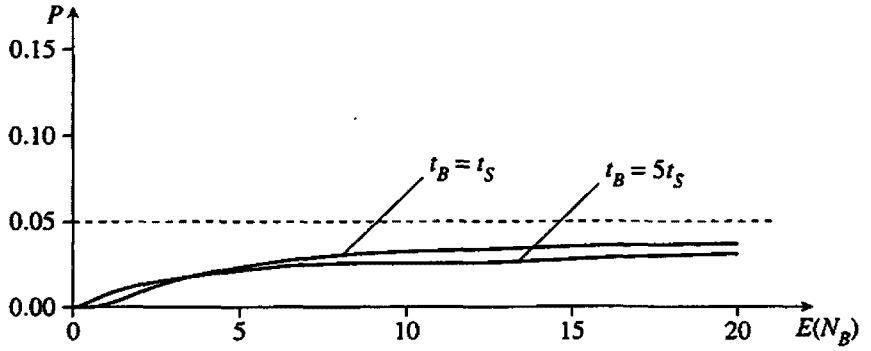

FIGURE 19.17 — Type I error rates for the nonrandomized exact test

2557 **EXAMPLE**

2558 **Problem**: A 6000-s blank measurement is performed on a proportional counter and 108 beta
2559 counts are observed. A test source is to be counted for 3000 s. Estimate the critical value of the
2560 net count when $\alpha = 0.05$.

2561 **Solution**: Formula A gives the result

2562
$$S_C = z_{1-\alpha}\sqrt{N_B \frac{t_S}{t_B}\left(1 + \frac{t_S}{t_B}\right)}$$
$$= 1.645\sqrt{108\left(\frac{3000}{6000}\right)\left(1 + \frac{3000}{6000}\right)}$$
$$= 14.8 \text{ counts.}$$

2563 Formula B is not recommended.

Formula C gives the result

$$S_C = \frac{z_{1-\alpha}^2 t_S}{2t_B} + z_{1-\alpha}\sqrt{\frac{z_{1-\alpha}^2 t_S^2}{4t_B^2} + N_B \frac{t_S}{t_B}\left(1 + \frac{t_S}{t_B}\right)}$$

$$= \frac{1.645^2(3000)}{2(6000)} + 1.645\sqrt{\frac{1.645^2(3000)^2}{4(6000)^2} + 108\left(\frac{3000}{6000}\right)\left(1 + \frac{3000}{6000}\right)}$$

$$= 15.5 \text{ counts.}$$

The Stapleton approximation (with $d = 0.4$) gives the result

$$S_C = d\left(\frac{t_S}{t_B} - 1\right) + \frac{z_{1-\alpha}^2}{4}\left(1 + \frac{t_S}{t_B}\right) + z_{1-\alpha}\sqrt{(N_B + d)\frac{t_S}{t_B}\left(1 + \frac{t_S}{t_B}\right)}$$

$$= 0.4\left(\frac{3000}{6000} - 1\right) + \frac{1.645^2}{4}\left(1 + \frac{3000}{6000}\right) + 1.645\sqrt{(108 + 0.4)\left(\frac{3000}{6000}\right)\left(1 + \frac{3000}{6000}\right)}$$

$$= 15.6 \text{ counts.}$$

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

$$S_C = 70 - (108)(3000 / 6000) = 16 \text{ counts.}$$

COMPARISONS

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 most complicated of the tests and requires either software or lookup tables to be practical, but it is the only one of the tests whose type I error rate is guaranteed not to exceed the chosen significance level. Achieving the chosen significance level exactly appears to require the randomized version of Nicholson's test.

19D.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

$$\Pr[\hat{S} \le S_C \mid X = x_D] = \beta \qquad (19.114)$$

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."

19D.3.1 The Minimum Detectable Net Instrument Signal

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. The minimum detectable value 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,

$$\Pr[\hat{S} \le S_C \mid S = S_D] = \beta \qquad (19.115)$$

where S denotes the true mean net signal.

19D.3.2 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

$$S_C = t_{1-\alpha}(\nu)\hat{\sigma}_0 \qquad (19.116)$$

Then, if the variance of $\hat{S}$ is constant at all concentrations, the minimum detectable value of the signal is given by

$$S_D = \delta_{\alpha,\beta,\nu}\sigma_0 \qquad (19.117)$$

where $\delta_{\alpha,\beta,\nu}$ denotes the non-centrality parameter of the non-central t-distribution with ν degrees of freedom. The parameter $\delta_{\alpha,\beta,\nu}$ is such that

$$t'_{\beta}(\nu, \delta_{\alpha,\beta,\nu}) = t_{1-\alpha}(\nu) \tag{19.118}$$

where $t'_{\beta}(\nu, \delta_{\alpha,\beta,\nu})$ denotes the β-quantile of the non-central t-distribution. The non-centrality parameter $\delta_{\alpha,\beta,\nu}$ may be approximated by

$$\delta_{\alpha,\beta,\nu} \approx t'\left(1 - \frac{1}{4\nu}\right) + z_{1-\beta}\sqrt{1 + \frac{t'^2}{2\nu}}, \qquad t' = t_{1-\alpha}(\nu) \tag{19.119}$$

which is based on an approximation for the non-central t distribution function (NBS 1964). When $\alpha = \beta = 0.05$ and $\nu \geq 4$, the non-centrality 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. An unbiased estimator for σ_0 is $\hat{\sigma}_0 / c_4$, where

$$c_4 = \frac{\Gamma\left(\frac{\nu+1}{2}\right)}{\Gamma\left(\frac{\nu}{2}\right)}\sqrt{\frac{2}{\nu}} \tag{19.120}$$

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

$$S_D = \delta_{\alpha,\beta,\nu}\frac{\hat{\sigma}_0}{c_4} \tag{19.121}$$

TABLE 19.5 — 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

which is approximately $2t_{0.95}(\nu)\hat{\sigma}_0$, or $2S_C$, when $\alpha = \beta = 0.05$ and $\nu \geq 4$. Values of c_4 for $\nu = 1$ to 40 are listed in Table 19.5.

Lower and upper confidence limits for S_D may be calculated using the equations

$$S_{D,\text{lower}} = \delta_{\alpha,\beta,\nu}\frac{\hat{\sigma}_0}{\sqrt{\chi^2_{1-\gamma/2}(\nu)/\nu}} \quad \text{and} \quad S_{D,\text{upper}} = \delta_{\alpha,\beta,\nu}\frac{\hat{\sigma}_0}{\sqrt{\chi^2_{\gamma/2}(\nu)/\nu}} \tag{19.122}$$

where $\chi^2_p(\nu)$ denotes the p-quantile of the chi-square distribution with ν degrees of freedom and γ denotes the desired confidence coefficient (see Table G.3 in Appendix G).

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

$$t'_\beta\left(\nu, \frac{S_D}{\sigma_D}\right) = t_{1-\alpha}(\nu)\frac{\sigma_0}{\sigma_D} \tag{19.123}$$

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. Set $S_D = t_{1-\alpha}(\nu)\sigma_0$
3. **repeat**
4. Set $\sigma_D = \sqrt{\sigma^2(\hat{S} \mid S = S_D)}$
5. Find the value of δ such that $t'_\beta(\nu,\delta) = t_{1-\alpha}(\nu)\,\sigma_0 / \sigma_D$
6. Set $h = S_D$
7. Set $S_D = \delta\sigma_D$
8. **until** $|S_D - h|$ is sufficiently small
9. **output** the solution S_D

The value of the non-centrality parameter δ in Step 5 may be approximated by

$$\delta \approx t'\left(1 - \frac{1}{4\nu}\right) + z_{1-\beta}\sqrt{1 + \frac{t'^2}{2\nu}}, \qquad t' = t_{1-\alpha}(\nu)\frac{\sigma_0}{\sigma_D} \tag{19.124}$$

When $\hat{\sigma}_0$ is determined by any means other than a statistical evaluation, S_D must be calculated differently.

19D.3.3 Poisson Counting

Another equation for S_D, which was described in Section 19.7.2.2, is

$$S_D = S_C + z_{1-\beta}\sqrt{\sigma^2(\hat{S} \mid S = S_D)} \tag{19.125}$$

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 function $\sigma^2(\hat{S} \mid S = S_D)$ can often be expressed in the form

$$\sigma^2(\hat{S}) = aS^2 + bS + c \tag{19.126}$$

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 approximately by

$$S_D = \frac{1}{I_\beta}\left(S_C + \frac{z_{1-\beta}^2 b}{2} + z_{1-\beta}\sqrt{bS_C + \frac{z_{1-\beta}^2 b^2}{4} + aS_C^2 + I_\beta c} \right) \tag{19.127}$$

where $I_\beta = 1 - z_{1-\beta}^2 a$.

Equation 19.125 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 19.4 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 19.127.

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 $R_B = 8 \times 10^{-4}$ cps, and the blank count time is $t_B = 6000$ s. Then $R_B t_B = 4.8$ counts. Using Table 19.4, 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 $\tilde{S}_C$ when making a detection decision, the value of $[S_C]$ used to calculate S_D is given by the following equation.

$$[S_C] = 0.4\left(\frac{t_S}{t_B} - 1\right) + \frac{1.645^2}{4}\left(1 + \frac{t_S}{t_B}\right) + 1.645\sqrt{(9 + 0.4)\frac{t_S}{t_B}\left(1 + \frac{t_S}{t_B}\right)} \tag{19.128}$$

So, if $t_S = t_B$, then $[S_C] = 8.48$ counts. If $R_B t_B$ (4.8 counts) were used as the blank count instead, $[S_C]$ would be only 6.66 counts.

2669 PURE POISSON COUNTING

2670 When the pure Poisson model is assumed and Formula A is used for the critical value, if the
2671 critical value, S_C, is determined from a sufficiently large total number of counts and if $\alpha = \beta$, the
2672 minimum detectable net signal S_D is given by the following simple equation.

$$S_D = z^2_{1-\beta} + 2S_C \tag{19.129}$$

2673 More generally, if Formula A or C is used to calculate the critical net count S_C, then S_D may be
2674 determined from Equation 19.127 using the following values for a, b, and c.

2675 $$a = 0 \qquad b = 1 \qquad c = R_B t_S \left(1 + \frac{t_S}{t_B} \right)$$

2676 The resulting formula for S_D is

$$S_D = S_C + \frac{z^2_{1-\beta}}{2} + z_{1-\beta} \sqrt{\frac{z^2_{1-\beta}}{4} + S_C + R_B t_S \left(1 + \frac{t_S}{t_B} \right)} \tag{19.130}$$

2677 As previously noted, counting data never follow the Poisson model exactly. Variable factors such
2678 as source geometry and placement, counting efficiency, and subsampling variance tend to
2679 increase a, while interferences and background instability tend to increase c.

2680 THE STAPLETON APPROXIMATION

2681 When the Stapleton approximation is used for S_C, the minimum detectable net count S_D may be
2682 calculated using Equation 19.130, but when the Poisson model is valid, a better estimate is given
2683 by the formula

$$S_D = \frac{(z_{1-\alpha} + z_{1-\beta})^2}{4} \left(1 + \frac{t_S}{t_B} \right) + (z_{1-\alpha} + z_{1-\beta}) \sqrt{R_B t_S \left(1 + \frac{t_S}{t_B} \right)} \tag{19.131}$$

Equation 19.131 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 19.6). It is recommended by ISO 11929-1 (ISO 2000a) in a slightly different but equivalent form.

When $\alpha = \beta = 0.05$ and $t_B = t_S$, the preceding equation becomes

$$S_D = 5.41 + 4.65\sqrt{R_B t_S} \tag{19.132}$$

The Stapleton approximations for S_C and S_D give very predictable type I and type II errors when the only measurement variance is Poisson.

When the Poisson model is incomplete because of excess relative variance ($a > 0$), one can use Equation 19.127 with appropriate values for a, b, and c. However, a somewhat better estimate of S_D can be obtained. The calculation is more involved.

$$S_D = \frac{b'^2 - 2a'c' + b'\sqrt{b'^2 - 4a'c'}}{2a'^2} - R_B t_S \tag{19.133}$$

where

$$a' = 1 - \frac{z_{1-\beta}^2 a}{4}$$

$$b' = 2\sqrt{R_B t_S} + z_{1-\alpha}\sqrt{1 + \frac{t_S}{t_B}}$$

$$c' = R_B t_S + \frac{z_{1-\alpha}^2 - z_{1-\beta}^2}{4}\left(1 + \frac{t_S}{t_B}\right) + z_{1-\alpha}\sqrt{R_B t_S\left(1 + \frac{t_S}{t_B}\right)}$$

PRECISE CALCULATION OF S_D

When the Poisson model is valid, 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 the expression:

$$\text{Power} = 1 - \exp(-R_B(t_S + t_B) - S) \sum_{n=0}^{\infty} \frac{(R_B t_B)^n}{n!} \sum_{k=0}^{\lfloor y_C(n) \rfloor} \frac{(R_B t_S + S)^k}{k!} \tag{19.134}$$

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 19.134, the value of S_D may be determined using an iterative algorithm, such as Newton's method or bisection, which calculates the power at various trial values of S until the correct value is found where the power equals $1 - \beta$ (e.g. see Burden and Faires 1993).

A procedure of the type described above generated the true values of S_D for Table 19.6, 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 net count, not the upper bound [N_B]. The use of [N_B] would produce larger estimates.

PRECISE CALCULATION OF x_D

Suppose the analyte concentration X is calculated by dividing the net signal S by the sensitivity A, where A varies considerably or there is considerable subsampling variance, but the signal is otherwise adequately described by the Poisson model. If one can assume that A has a particular distribution, such as a rectangular or triangular distribution, then it is possible to calculate x_D precisely in software, although the mathematics is less straightforward than that needed to calculate S_D in the preceding section. At any specified concentration x, the detection power equals

$$\text{Power} = 1 - e^{-R_B t_B} \sum_{n=0}^{\infty} \frac{(R_B t_B)^n}{n!} \sum_{k=0}^{\lfloor y_C(n) \rfloor} f(k;x) \tag{19.135}$$

where $f(k;x)$ is the probability that the gross count will equal k when the concentration is x. For example, if A has a rectangular distribution with mean μ_A and half-width δ, then

$$f(k;x) = \frac{P(k+1, R_B t_S + (\mu_A + \delta)x) - P(k+1, R_B t_S + (\mu_A - \delta)x)}{2\delta x} \tag{19.136}$$

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).

TABLE 19.6 — Estimated and true values of S_D ($t_B = t_S$)

Mean Blank Count	Formula A		Formula C		Stapleton	
	Estimated	True	Estimated	True	Estimated	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

A precise power calculation of this type was performed to evaluate the results derived in the example in Attachment 19E assuming an approximately normal distribution for the subsampling error. The assumption of a normal distribution is nonsensical unless the relative standard deviation of A is small (because A is positive), and in the latter case, the assumption of a triangular distribution, or even a rectangular distribution, gives approximately the same result.

19D.4 References

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ATTACHMENT 19E
Example Calculations

19E.1 Overview

The following example shows how to calculate the combined standard uncertainty, critical net signal, minimum detectable concentration (MDC), and minimum quantifiable concentration (MQC) for a typical radioanalytical measurement.

19E.2 Sample Collection and Analysis

A soil sample is analyzed for $^{239/240}Pu$ and ^{238}Pu by alpha 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 0.2 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, including contributions from repeatability, linearity, day-to-day variability, and the balance calibration, is estimated to be 2.2×10^{-4} g.
- A 1-mL aliquant of ^{242}Pu tracer is added to the test portion. The concentration of the tracer solution has previously been measured as 0.0705 Bq mL^{-1} with a standard uncertainty of 0.0020 Bq mL^{-1} 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 spectrometer.
- The efficiency of the spectrometer for the chosen geometry, which is assumed to be constant over the range of alpha energies of interest, 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 mean activity concentration, or massic activity, of ^{238}Pu in the 2-kg sample (dry weight) at the time of collection.

19E.3 The Measurement Model

The following notation will be used:

M_S	is the mass of the test portion (0.5017 g)
T	is the tracer activity concentration (0.1205 Bq mL^{-1})
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 alphas 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 counting efficiency
Y	is the plutonium chemical yield fraction
F_S	is the subsampling factor (estimated as 1.00 with a Type B standard uncertainty of 0.05)
X	is the ^{238}Pu activity concentration 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:

$$D = e^{-\lambda t_D} \frac{1 - e^{-\lambda t_S}}{\lambda t_S}$$

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

$$D = e^{-\lambda(t_D + t_S/2)}$$

The half-lives of ^{238}Pu and ^{242}Pu are 87.75 y and 375,800 y, respectively. So,

$$D_{238} = \exp\left(\frac{-\ln 2}{87.75 \cdot 365.25 \cdot 86{,}400} \left(3{,}911{,}400 + \frac{60{,}000}{2} \right) \right) = 0.9990$$

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 alphas 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

$$Y = \frac{N_{S,242}/t_S - N_{B,242}/t_B}{TV_t \varepsilon R_{242} D_{242}}$$

Then the following model is used to estimate the measurand.

2853
$$X = \frac{N_{S,238}/t_S - N_{B,238}/t_B}{M_S Y \varepsilon R_{238} D_{238} F_S}$$

2854 When numerical values are inserted,

$$Y = \frac{967/60{,}000 - 2/60{,}000}{0.0705 \cdot 1 \cdot 0.2805 \cdot 0.98 \cdot 1} = 0.82990$$

$$X = \frac{75/60{,}000 - 0/60{,}000}{0.5017 \cdot 0.82990 \cdot 0.2805 \cdot 0.98 \cdot 0.9990 \cdot 1.00} = 0.010932 \text{ Bq g}^{-1}$$

(or 10.932 Bq kg^{-1})

2855 **19E.4 The Combined Standard Uncertainty**

2856 The efficiency ε effectively cancels out of the equation for X, because it is multiplied by the yield
2857 Y and also appears as a factor in the denominator of the expression for Y (see also Section
2858 19.6.5). Therefore, the uncertainty of ε has no effect on the uncertainty of X. When using the
2859 uncertainty propagation formula to calculate the combined standard uncertainty of X, one might
2860 include a covariance term for $u(Y,\varepsilon)$ to account for the relationship between the measured values
2861 of Y and ε, but it is simpler to treat $Y\varepsilon$ as one variable. Application of the uncertainty propagation
2862 formula (Section 19.5.3) to the equations above then gives the following:

2863
$$u_c^2(Y\varepsilon) = \frac{u^2(N_{S,242})/t_S^2 + u^2(N_{B,242})/t_B^2}{T^2 V_t^2 R_{242}^2 D_{242}^2} + (Y\varepsilon)^2 \left(\frac{u^2(T)}{T^2} + \frac{u^2(V_t)}{V_t^2} + \frac{u^2(R_{242})}{R_{242}^2} \right)$$

2864
$$u_c^2(X) = \frac{u^2(N_{S,238})/t_S^2 + u^2(N_{B,238})/t_B^2}{M_S^2 (Y\varepsilon)^2 R_{238}^2 D_{238}^2} + X^2 \left(\frac{u^2(M_S)}{M_S^2} + \frac{u^2(Y\varepsilon)}{(Y\varepsilon)^2} + \frac{u^2(R_{238})}{R_{238}^2} + \frac{u^2(F_S)}{F_S^2} \right)$$

2865 All other input estimates are assumed to be uncorrelated.

2866 Note that $u^2(F_S)$ is the subsampling variance associated with taking a small test portion
2867 (0.5017 g) from a much larger sample (2 kg). A default value is used here for this variance
2868 component. However, Appendix F provides more information about subsampling errors and
2869 methods for estimating their variances.

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 19C.3 of Attachment 19C). So, for example, $u(N_{B,238})$ equals one, not zero.

Table 19.7 summarizes the input estimates and their standard uncertainties.

TABLE 19.7 — 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
T	0.0705	0.0020	Bq mL^{-1}	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	0.05	none	B
D_{238}	0.9990	Negligible	none	B
D_{242}	1.0000	Negligible	none	B

Other possible sources of uncertainty in alpha spectrometry measurements include the following:

- 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
- changing instrument background
- dependence of counting efficiency on alpha energy

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 numerical values are inserted into the formulas

$$u_c^2(Y\varepsilon) = \frac{968/60{,}000^2 + 3/60{,}000^2}{0.0705^2 \cdot 1^2 \cdot 0.98^2 \cdot 1^2} + (0.82990 \cdot 0.2805)^2 \left(\frac{0.0020^2}{0.0705^2} + \frac{0.0057^2}{1^2} + \frac{0.01155^2}{0.98^2} \right)$$

$$= 0.0001094007 = 0.01046^2$$

and

$$u_c^2(X) = \frac{76/60{,}000^2 + 1/60{,}000^2}{0.5017^2 \cdot (0.82990 \cdot 0.2805)^2 \cdot 0.98^2 \cdot 0.9990^2} + 0.010932^2 \left(\frac{(2.2 \times 10^{-4})^2}{0.5017^2} + \frac{0.01046^2}{0.82990^2 \cdot 0.2805^2} + \frac{0.01155^2}{0.98^2} + \frac{0.05^2}{1.00^2} \right)$$

$$= 2.1926 \times 10^{-6} = 0.0014808^2$$

So, $u_c(X) = 0.00148$ Bq g^{-1} or 1.48 Bq kg^{-1}. If the concentration is to be reported with an expanded uncertainty calculated from the combined standard uncertainty $u_c(X)$ and a coverage factor $k = 2$, the result should appear (in SI units) as 10.9 ± 3.0 Bq kg^{-1} (dry weight).

19E.5 The Critical Net Count

Chapter 19 discusses several methods for estimating the critical net count S_C. In this example, the observed blank count is zero; so, the mean blank count is obviously very low, and nonnormal Poisson counting statistics may be assumed. Sections 19E.5.1 through 19E.5.4 below show how to apply the formulas discussed in Section 19D.2.2 for Poisson counting measurements, assuming a significance level of $\alpha = 0.05$.

19E.5.1 Formula A

Formula A is not recommended when the blank count is extremely low, as in this example. However, if Formula A is used, it gives the following estimate of the critical value of the net count.

$$S_C = z_{1-\alpha}\sqrt{N_{B,238}\frac{t_S}{t_B}\left(1+\frac{t_S}{t_B}\right)}$$

2900

$$= 1.645\sqrt{(0)(1)(2)}$$

$$= 0 \text{ counts}$$

2901 Since the net count 75 exceeds the critical net count 0, the analyte ^{238}Pu is considered "detected."

2902 19E.5.2 Formula C

2903 Using Formula C, one obtains

$$S_C = \frac{z_{1-\alpha}^2 t_S}{2t_B} + z_{1-\alpha}\sqrt{\frac{z_{1-\alpha}^2 t_S^2}{4t_B^2} + N_{B,238}\frac{t_S}{t_B}\left(1+\frac{t_S}{t_B}\right)}$$

$$= \frac{1.645^2}{2}(1) + 1.645\sqrt{\frac{1.645^2}{4}(1)^2 + (0)(1)(2)}$$

$$= 2.71 \text{ counts}$$

2904 Since 75 > 2.71, the analyte is considered detected.

2905 19E.5.3 The Stapleton Approximation

2906 Using the Stapleton approximation, the critical net count is calculated as follows.

$$S_C = 0.4\left(\frac{t_S}{t_B} - 1\right) + \frac{z_{1-\alpha}^2}{4}\left(1+\frac{t_S}{t_B}\right) + z_{1-\alpha}\sqrt{(N_{B,238}+0.4)\frac{t_S}{t_B}\left(1+\frac{t_S}{t_B}\right)}$$

$$= 0.4(0) + \frac{1.645^2}{4}(2) + 1.645\sqrt{(0+0.4)(1)(2)}$$

$$= 2.82 \text{ counts}$$

2907 Since 75 > 2.82, the analyte is considered detected.

2908 19E.5.4 Exact Test

2909 When the exact test is used, the critical value of the source count $N_{S,238}$ is the smallest nonnega-
2910 tive integer y_C such that

$$\sum_{k=0}^{y_C} \binom{N_{B,238}+k}{N_{B,238}} \left(\frac{t_S}{t_B+t_S}\right)^k \geq (1-\alpha)\left(1+\frac{t_S}{t_B}\right)^{N_{B,238}+1} \qquad (19.144)$$

2911 First the right-hand side is calculated:

2912 $$(1-\alpha)\left(1+\frac{t_S}{t_B}\right)^{N_{B,238}+1} = (0.95)(2)^{0+1} = 1.90$$

2913 Then, terms of the sum on the left-hand side are accumulated until the total is at least 1.90. The
2914 iteration stops at $k = 4$, when the sum reaches 1.9375 (illustrated below).

2915
2916
2917
2918
2919
2920

k	k^{th} Term	Sum
0	1	1
1	0.5	1.5
2	0.25	1.75
3	0.125	1.875
4	0.0625	1.9375

2921 Thus, the critical value of the total count is $y_C = 4$, which may also be found in Table G.4 in
2922 Appendix G. Since the observed count $N_{S,238} = 75$ exceeds the critical count, one concludes that
2923 the sample contains a positive amount of ^{238}Pu.

2924 The critical net count S_C in this case is also 4, because the blank count is zero. Note that this
2925 value of S_C is the most conservative of the critical values calculated in this example.

19E.6 The Minimum Detectable Concentration

Assume the specified probability of a type II error at the minimum detectable concentration is $\beta = 0.05$. The following describes a conservative approach to the estimation of the nominal MDC for the analytical process.

Let R_B denote the mean blank count rate for the ^{238}Pu region of interest. Suppose a total of 21 counts are accumulated in the ^{238}Pu region of interest during ten 60,000-s blank measurements. The estimated blank count rate is then

$$R_B = \frac{21}{600{,}000} = 3.5 \times 10^{-5} \text{ cps}$$

This estimate has a moderately large relative standard uncertainty (approximately 22%), but detection decisions are based on the results of shorter measurements (60,000 s, not 600,000 s), which will vary even more. So, a conservative upper bound $[N_B]$ will be used for the blank count, as suggested in Section 19D.3.2 of Attachment 19D. A method for calculating the critical gross count can be adapted to calculate the largest value of the blank count that is likely to be observed given the assumption of a mean blank count rate of 3.5×10^{-5} cps. For the current problem, Table 19.4 will be used, with $R_B t_B$ replacing $R_B t_S$ and $[N_B]$ replacing y_C in the column headings. Since the value of $R_B t_B$ is 2.1, which lies between 1.970 and 2.613, Table 19.4 shows that the required value is $[N_B] = 5$. Therefore, one expects the number of blank counts observed in 60,000 s (t_B) to be no greater than 5. So, the MDC will be calculated here using a critical value $[S_C]$ based on the assumption of a blank count $[N_B] = 5$.

The overall sensitivity for the measurement process is the product $A = t_S M_S Y \varepsilon R_{238} D_{238}$. Since the most variable factor in this product by far is the chemical yield Y, a conservative lower bound for A may be found by estimating the β-quantile (5th percentile) of Y and multiplying it by estimated values of the other factors. Assume that historical data show that the 5th percentile of Y is approximately 0.60. Then with the measured efficiency 0.2805, nominal test portion mass 0.5 g, and estimated values for the ROI fraction 0.98 and decay factor 0.999, the 5th percentile of A is estimated as

$$a_\beta = a_{0.05} = (60{,}000)(0.60)(0.2805)(0.5)(0.98)(0.999) = 4943 \text{ g s}$$

The approximation formulas given in the chapter will be used and the results will be compared to the results obtained from a precise power calculation using the value a_β for the sensitivity and with the assumptions that the mean blank count rate is $R_B = 3.5 \times 10^{-5}$ cps and that the subsampling error is approximately normal.

2957 The following values, which appear in several formulas, are calculated first.

$$c = R_B t_S \left(1 + \frac{t_S}{t_B} \right) = (3.5 \times 10^{-5})(60{,}000)(1 + 1) = 4.2 \text{ counts}$$

2958

$$I_\beta = 1 - z_{1-\beta}^2 \varphi_{Samp}^2 = 1 - (1.645)^2 (0.05)^2 = 0.993236$$

$$I_\beta c = (0.993236)(4.2) = 4.172 \text{ counts}$$

2959 19E.6.1 Formula A

2960 Assuming the net signal is approximately normal at the MDC, the value of the MDC may be
2961 approximated by

2962 $$x_D = \frac{1}{a_\beta I_\beta} \left([S_C] + \frac{z_{1-\beta}^2}{2} + z_{1-\beta} \sqrt{\frac{z_{1-\beta}^2}{4} + [S_C] + \varphi_{Samp}^2 [S_C]^2 + I_\beta c} \right)$$

2963 where $[S_C]$ denotes the critical net count calculated using $[N_B]$ as the blank count and φ_{Samp}^2
2964 denotes the subsampling variance, which also equals $u^2(F_S)$. When Formula A is used, $[S_C]$ is

2965 $$[S_C] = z_{1-\alpha} \sqrt{[N_B] \frac{t_S}{t_B} \left(1 + \frac{t_S}{t_B} \right)} = 1.645 \sqrt{(5)(1)(1 + 1)} = 5.201 \text{ counts}$$

2966 and the minimum detectable concentration is

2967 $$x_D = \frac{1}{a_\beta I_\beta} \left([S_C] + \frac{z_{1-\beta}^2}{2} + z_{1-\beta} \sqrt{\frac{z_{1-\beta}^2}{4} + [S_C] + \varphi_{Samp}^2 [S_C]^2 + I_\beta c} \right)$$

$$= \frac{1}{(4943)(0.993236)} \left(5.201 + \frac{1.645^2}{2} + 1.645 \sqrt{\frac{1.645^2}{4} + 5.201 + (0.05)^2 (5.201)^2 + 4.172} \right)$$

$$= 0.0024 \text{ Bq g}^{-1} \quad \text{or} \quad 2.4 \text{ Bq kg}^{-1}$$

2968 If the calculation is repeated with $R_B t_B = 2.1$ substituted for $[N_B] = 5$ as the blank count used to
2969 calculate the critical value, the resulting value of x_D is 1.9 Bq kg^{-1}. A precise power calculation
2970 shows that the actual value of x_D is 2.1 Bq kg^{-1}.

2971 19E.6.2 Formula C

2972 Using Formula C, one obtains

$$[S_C] = \frac{z_{1-\alpha}^2 t_S}{2t_B} + z_{1-\alpha}\sqrt{\frac{z_{1-\alpha}^2 t_S^2}{4t_B^2} + [N_B]\frac{t_S}{t_B}\left(1 + \frac{t_S}{t_B}\right)}$$

$$= \frac{1.645^2}{2}(1) + 1.645\sqrt{\frac{1.645^2}{4}(1)^2 + 10}$$

$$= 6.727 \text{ counts}$$

2973 Then the minimum detectable concentration is

$$x_D = \frac{1}{a_\beta I_\beta}\left([S_C] + \frac{z_{1-\beta}^2}{2} + z_{1-\beta}\sqrt{\frac{z_{1-\beta}^2}{4} + [S_C] + \varphi_{Samp}^2[S_C]^2 + I_\beta c}\right)$$

2974

$$= \frac{1}{(4943)(0.993236)}\left(6.727 + \frac{1.645^2}{2} + 1.645\sqrt{\frac{1.645^2}{4} + 6.727 + (0.05)^2(6.727)^2 + 4.172}\right)$$

$$= 0.0028 \text{ Bq g}^{-1} \quad \text{or} \quad 2.8 \text{ Bq kg}^{-1}$$

2975 If the critical value is calculated using $R_B t_B = 2.1$ instead of $[N_B] = 5$, the resulting value of x_D is
2976 2.3 Bq kg^{-1}. A precise power calculation gives the value $x_D = 2.5$ Bq kg^{-1}.

2977 19E.6.3 The Stapleton Approximation

2978 When the Stapleton approximation is used, the critical net count is

$$[S_C] = 0.4\left(\frac{t_S}{t_B} - 1\right) + \frac{z_{1-\alpha}^2}{4}\left(1 + \frac{t_S}{t_B}\right) + z_{1-\alpha}\sqrt{([N_B] + 0.4)\frac{t_S}{t_B}\left(1 + \frac{t_S}{t_B}\right)}$$

$$= 0.4(0) + \frac{1.645^2}{4}(2) + 1.645\sqrt{(5 + 0.4)(1)(2)}$$

$$= 6.758 \text{ counts}$$

Then the minimum detectable concentration may be approximated by

$$x_D = \frac{1}{a_\beta I_\beta}\left([S_C] + \frac{z^2_{1-\beta}}{2} + z_{1-\beta}\sqrt{\frac{z^2_{1-\beta}}{4} + [S_C] + \varphi^2_{Samp}[S_C]^2 + I_\beta c}\right)$$

$$= \frac{1}{(4943)(0.993236)}\left(6.758 + \frac{1.645^2}{2} + 1.645\sqrt{\frac{1.645^2}{4} + 6.758 + (0.05)^2(6.758)^2 + 4.172}\right)$$

$$= 0.0028 \text{ Bq g}^{-1} \quad \text{or} \quad 2.8 \text{ Bq kg}^{-1}$$

When $R_B t_B$ is substituted for $[N_B]$ in the calculation of the critical value, the resulting value of x_D is 2.4 Bq kg^{-1}.

Alternatively, the longer calculation given in Section 19D.3.3 of Attachment 19D may be used.

$$x_D = \frac{1}{a_\beta}\left(\frac{b'^2 - 2a'c' + b'\sqrt{b'^2 - 4a'c'}}{2a'^2} - R_B t_S\right)$$

where

$$a' = 1 - \frac{z^2_{1-\beta}\varphi^2_{Samp}}{4} = 0.99831$$

$$b' = 2\sqrt{R_B t_S} + z_{1-\alpha}\sqrt{1 + \frac{t_S}{t_B}} = 5.2244$$

$$c' = R_B t_S + \frac{z^2_{1-\alpha} - z^2_{1-\beta}}{4}\left(1 + \frac{t_S}{t_B}\right) + z_{1-\alpha}\sqrt{R_B t_S\left(1 + \frac{t_S}{t_B}\right)} = 5.4709$$

Then

$$x_D = \frac{5.2244^2 - 2(0.99831)(5.4709) + (5.2244)\sqrt{5.2244^2 - 4(0.99831)(5.4709)}}{2(0.99831)^2(4943)} - \frac{2.1}{4943}$$

$$= 0.0025 \text{ Bq g}^{-1} \quad \text{or} \quad 2.5 \text{ Bq kg}^{-1}$$

A precise power calculation gives the value $x_D = 2.5$ Bq kg^{-1}.

2992 19E.6.4 Exact Test

2993 When the exact test for detection is used, the critical gross count $[y_C]$ equals the smallest nonneg-
2994 ative integer n such that

2995 $$\sum_{k=0}^{n} \binom{[N_B]+k}{[N_B]} \left(\frac{t_S}{t_B+t_S}\right)^k \geq (1-\alpha)\left(1+\frac{t_S}{t_B}\right)^{[N_B]+1}$$

2996 The right-hand side of the inequality is found as follows

2997 $$\text{RHS} = (1-0.05)(1+1)^{5+1} = 60.8$$

2998 The value of the left-hand side exceeds 60.8 when n equals 12

2999 $$\text{LHS} = \binom{5}{5} + \binom{6}{5}\frac{1}{2} + \binom{7}{5}\frac{1}{4} + \cdots + \binom{17}{5}\frac{1}{4096} = 60.92$$

3000 Therefore,

3001 $$[y_C] = 12 \text{ counts} \quad \text{and} \quad [S_C] = [y_C] - [N_B]\frac{t_S}{t_B} = 7 \text{ counts}$$

3002 So,

3003 $$x_D = \frac{1}{a_\beta I_\beta}\left([S_C] + \frac{z_{1-\beta}^2}{2} + z_{1-\beta}\sqrt{\frac{z_{1-\beta}^2}{4} + [S_C] + \varphi_{\text{Samp}}^2[S_C]^2 + I_\beta c}\right)$$
$$= \frac{1}{(4943)(0.993236)}\left(7 + \frac{1.645^2}{2} + 1.645\sqrt{\frac{1.645^2}{4} + 7 + (0.05)^2(7)^2 + 4.172}\right)$$
$$= 0.0029 \text{ Bq g}^{-1} \quad \text{or} \quad 2.9 \text{ Bq kg}^{-1}$$

3004 The result of the precise calculation is $x_D = 2.8$ Bq kg^{-1}.

19E.7 The Minimum Quantifiable Concentration

For the purpose of this example, the MQC is defined to be the analyte concentration x_Q at which the relative standard deviation of the measured result is $1 / k_Q$, where $k_Q = 10$. Calculation of x_Q requires knowledge of the relative standard deviation of the measured sensitivity when the true sensitivity is $A = a_{0.05}$. Assume for this example that the relative standard deviation is $\varphi_{\hat{A}} \approx 0.051$ (5.1%) at $A = a_{0.05} = 4943$. Then

$$x_Q = \frac{k_Q^2}{2a_{0.05}I_Q}\left(1 + \sqrt{1 + \frac{4I_Q R_B t_S}{k_Q^2}\left(1 + \frac{t_S}{t_B}\right)}\right)$$

where

$$I_Q = 1 - k_Q^2(\varphi_{\hat{A}}^2 + \varphi_{\text{Samp}}^2) = 1 - 10^2\,(0.051^2 + 0.05^2) = 0.4899$$

Then

$$x_Q = \frac{10^2}{2(4943)(0.4899)}\left(1 + \sqrt{1 + \frac{4(0.4899)(3.5 \times 10^{-5})(60{,}000)}{10^2}(1 + 1)}\right)$$

$$= 0.042 \text{ Bq g}^{-1} \quad \text{or} \quad 42 \text{ Bq kg}^{-1}$$

The MQC is substantially increased by the measurement variance of the sensitivity $\hat{A}$ and the subsampling variance. Without them the minimum quantifiable concentration would be only 21 Bq kg^{-1}. Note also that if either the relative standard deviation of $\hat{A}$ or the subsampling standard deviation were 0.1 or more, the MQC would be infinite.

ATTACHMENT 19F
Tests for Normality

19F.1 Purpose

Many common statistical hypothesis tests are based on the assumption that data are normally distributed. Normality is often assumed by default, but, since some tests may not perform well with data that are not normal, it is often important to check the validity of the assumption. Performing a test for normality cannot prove that data are normally distributed, but it may produce strong evidence that they are not.

There are a number of tests for normality. Each test requires a random sample $Y_1, Y_2, \ldots, Y_n$ from the distribution being checked. Whatever test is used, it is a good idea to plot the data for visual inspection. The normal probability plot described in Section 19F.2 is useful for this purpose.

One of the most powerful tests for normality is the Shapiro-Wilk test, but it is difficult to implement manually. EPA QA/G-9 recommends the Shapiro-Wilk test when the sample size n is less than 50, and either Filliben's statistic or the studentized range test when $n > 50$ (EPA 1998). In fact, if software for the Shapiro-Wilk test is not available, then Filliben's statistic may be used in all cases for which critical values are available. Instructions for computing and using Filliben's statistic are given in Section 19F.3.

19F.2 Normal Probability Plots

A normal probability plot is a graph of the observed quantiles of a data set against the corresponding quantiles of a standard normal distribution. If the data are normally distributed and the data set is large enough (more than about 10 values), the plotted points should lie approximately on a straight line. A preliminary decision about the distribution of the data may be based on inspection of the graph. Normal probability plots may be produced manually, although software is generally needed to make plots of large data sets feasible.

Manual construction of a normal probability plot is easier when pre-printed normal probability paper is available (see Figure 19.18 at the end of this attachment).

To plot a set of data on normal probability paper, perform the following steps (EPA 1998).

1. Arrange the data in ascending order:

$$Y_{(1)} \le Y_{(2)} \le \cdots \le Y_{(n)}$$

2. Label the vertical axis to encompass all values between $Y_{(1)}$ (the minimum) and $Y_{(n)}$ (the maximum).

3. For each i compute the cumulative frequency F_i of the value $Y_{(i)}$, which is defined as the number of values in the data set that are less than or equal to $Y_{(i)}$. (Note that $F_i \geq i$.)

4. Compute the horizontal coordinate $X_i = F_i / (n + 1) \times 100\%$ for each i.

5. Plot each ordered pair $(X_i, Y_{(i)})$ at the appropriate location on the grid.

To plot a set of data on ordinary graph paper, perform Steps 1–3 above followed by Steps 4′–6′ below.

4′. For each i, determine the quantile $X_i = z_{F_i/(n+1)}$ of the standard normal distribution (see for example Table G.1).

5′. Label the horizontal axis to encompass all values between X_1 and X_n.

6′. Plot each ordered pair $(X_i, Y_{(i)})$.

The latter version of the procedure can be adapted to construct probability plots for other types of distributions. Only Step 4′ must change, since X_i is required to be a quantile of the appropriate distribution.

EXAMPLE

Problem: Given the data set

123 122 124 118 118 122 121 117 125 119

construct a normal probability plot using normal probability paper.

Solution:

Step 1 Sort the 10 values:

117 118 118 119 121 122 122 123 124 125

Step 2 Label the vertical axis to encompass the values from 117 to 125.

Step 3 For each i compute the cumulative frequency F_i of $Y_{(i)}$ (see the table below).

Step 4 For each i compute $X_i = (F_i / 11) \times 100\%$ and plot $(X_i, Y_{(i)})$.

i	1	2	3	4	5	6	7	8	9	10
$Y_{(i)}$	117	118	118	119	121	122	122	123	124	125
F_i	1	3	3	4	5	7	7	8	9	10
X_i	9.1%	27.3%	27.3%	36.4%	45.5%	63.6%	63.6%	72.7%	81.8%	90.9%

The results are shown as a normal probability plot in Figure 19.18.

19F.3 Filliben's Statistic

Filliben's statistic is derived from the concept of the normal probability plot and is often called the "normal probability plot correlation coefficient." The use of the statistic makes the interpretation of the probability plot less subjective, although a visual inspection of the plot is still recommended. The procedure for calculating and using the statistic is given below (Filliben 1975).

1. Choose the significance level α.

2. Arrange the data in ascending order.

$$Y_{(1)} \le Y_{(2)} \le \cdots \le Y_{(n)}$$

3. Compute the quantities $\overline{Y}$ and S as follows.

$$\overline{Y} = \frac{1}{n}\sum_{i=1}^{n} Y_i \qquad S = \sqrt{\sum_{i=1}^{n} (Y_i - \overline{Y})^2}$$

4. For $i = 1, 2, \ldots, n$, compute

3082
$$m_i = \begin{cases} 1 - 0.5^{1/n}, & i = 1 \\ (i - 0.3175)/(n + 0.365), & i = 2,3,\ldots,n-1 \\ 0.5^{1/n}, & i = n \end{cases}$$

3083 and let M_i be the m_i-quantile of the standard normal distribution z_{m_i}. (Table G.1 in
3084 Appendix G may be interpolated to obtain approximate values of these quantiles.)

3085 5. Compute $c_n = \sqrt{\sum_{i=1}^{n} M_i^2}$.

3086 6. Compute Filliben's statistic r (the normal probability plot correlation coefficient).

3087
$$r = \frac{\sum_{i=1}^{n} Y_{(i)} M_i}{c_n S}$$

3088 7. Determine a critical value from Table G.5. If r is less than the critical value, conclude that
3089 the data are not normally distributed.

3090 **EXAMPLE**

3091 **Problem:** Determine whether the values

3092 123 122 124 118 118 122 121 117 125 119

3093 appear to come from a normal distribution. Use the significance level 0.05.

3094 **Solution:**

3095 Step 1 The significance level is specified to be $\alpha = 0.05$.

3096 Step 2 Sort the 10 values:

117 118 118 119 121 122 122 123 124 125

3097 Step 3 Compute $\overline{Y} = \frac{1}{10}\sum Y_i = 120.9$ and

$$S = \sqrt{\sum (Y_i - 120.9)^2} = 8.301$$

3098 Step 4 For each i compute m_i and $M_i = z_{m_i}$ (see the table below). (The quantiles M_i in this example have been computed without using Table G.1.)

3099 Step 5 Compute $c_n = \sqrt{\sum_{i=1}^{10} M_i^2} = \sqrt{7.575} = 2.752$.

3100 Step 6 Compute $r = \frac{\sum_{i=1}^{10} Y_{(i)} M_i}{c_n S} = \frac{22.37}{(2.752)(8.301)} = 0.979$.

3101 Step 7 Table G.5 shows that the critical value for $n = 10$ and $\alpha = 0.05$ is 0.917. Since $0.979 \geq 0.917$, the data appear to be normally distributed.

i	1	2	3	4	5	6	7	8	9	10
$Y_{(i)}$	117	118	118	119	121	122	122	123	124	125
m_i	0.06697	0.1623	0.2588	0.3553	0.4518	0.5482	0.6447	0.7412	0.8377	0.9330
M_i	–1.499	–0.9849	–0.6470	–0.3711	–0.1212	0.1212	0.3711	0.6470	0.9849	1.499

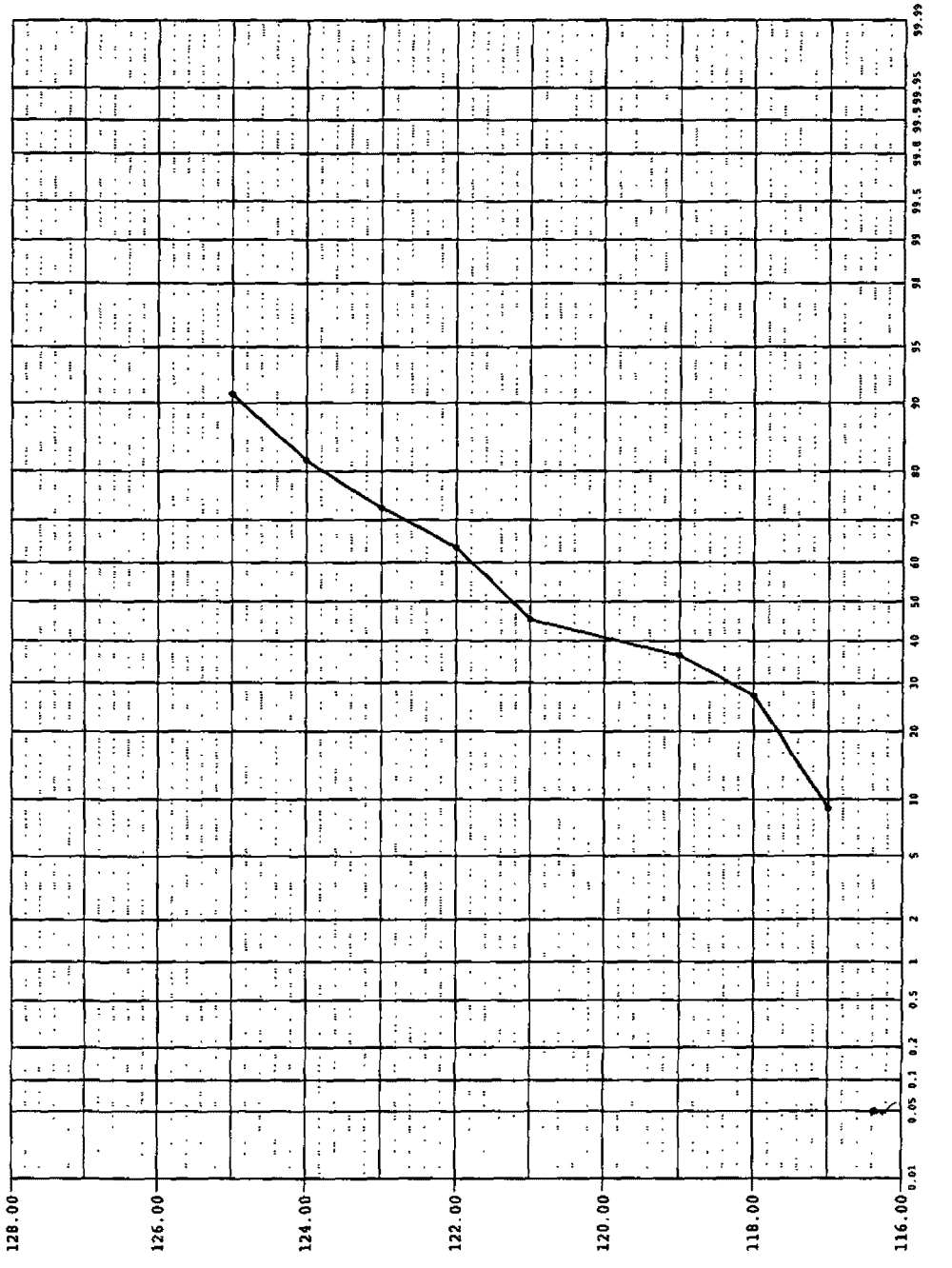

FIGURE 19.18 — Example: Normal probability plot

19F.4 References

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ATTACHMENT 19G
Balance Measurement Uncertainty

19G.1 Purpose

This attachment describes methods that may be used to evaluate balance measurement uncertainty. The relative standard uncertainty of a measurement made with a laboratory balance tends to be small if the balance is used properly, and it may even be considered negligible when compared to other uncertainties associated with radioanalysis (e.g., see Section 19.6.11, "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 balance is used to weigh a mass that is too small for it. Establishing reasonable acceptance criteria for balance quality control also requires an understanding of the sources of the measurement uncertainty.

19G.2 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.

19G.3 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 1993). 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.

A nested experimental design can also be used to evaluate both the repeatability and the day-to-day 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. Ideally one should use a mass near the capacity of the balance to obtain the most reliable estimate of day-to-day variability. The repeatability standard deviation is then estimated by

$$s_r = \sqrt{\frac{1}{K(J-1)} \sum_{k=1}^{K} \sum_{j=1}^{J} (x_{k,j} - \bar{x}_k)^2} \qquad (19.150)$$

where

s_r is the estimated repeatability standard deviation
J is the number of repetitions per day
K is the number of days
$x_{k,j}$ is the j^{th} result obtained on the k^{th} day
$\bar{x}_k$ is the average of all the results on the k^{th} day

The repeatability standard deviation determined by this method is a Type A standard uncertainty with $K(J-1)$ degrees of freedom.

19G.4 Environmental Factors

Given the experimental data from the preceding section, one may estimate the variability due to environmental factors (day-to-day variability) as follows.[29]

$$s_{Env}^2 = \frac{1}{K-1} \sum_{k=1}^{K} (\bar{x}_k - \bar{\bar{x}})^2 - \frac{s_r^2}{J} \qquad (19.151)$$

where

s_{Env}^2 is the estimated variance due to environmental factors
$\bar{\bar{x}}$ is the grand average of all the data (the average of the $\bar{x}_k$)

[29] 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 $\bar{x}_j$, may be assumed to have an F-distribution with $K - 1$ numerator degrees of freedom and $K(J - 1)$ denominator degrees of freedom.

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

$$\varphi_{Env} = \frac{s_{Env}}{M_{Check}} \tag{19.152}$$

where M_{Check} is the mass of the standard used in the experiment.

19G.5 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-g 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 1991). 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 measured mass due to calibration may be estimated as follows.

$$\varphi_{Cal} = \sqrt{\varphi_{Env}^2 + \frac{s_r^2 + a_{Cal}^2 / 6}{M_{Cal}^2}} \tag{19.153}$$

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
- a_{Cal} is the tolerance for the mass of the calibration standard
- 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 a_{Cal} are much smaller than M_{Cal}.

19G.6 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, 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.

19G.7 Air Buoyancy Corrections

Air buoyancy corrections have not often been performed in radiochemistry laboratories, but they are necessary for a realistic estimate of the standard uncertainty of a mass measurement, especially when the material being weighed has a low density. 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.

$$m = I_{\text{Net}} B \tag{19.154}$$

where

$$B = \frac{1 - \rho_{A,C} / \rho_C}{1 - \rho_{A,M} / \rho_M} \tag{19.155}$$

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
- $\rho_{A.M}$ is the density of the air at the time the material is weighed

3211 ρ_C is the density of the calibration mass standard
3212 $\rho_{A,C}$ is the density of the air at the time of calibration

3213 The standard uncertainty of B may be obtained as follows.

$$\frac{u^2(B)}{B^2} = \frac{\dfrac{u^2(\rho_{A,C})}{\rho_{A,C}^2} - 2\dfrac{u(\rho_{A,C},\rho_C)}{\rho_{A,C}\rho_C} + \dfrac{u^2(\rho_C)}{\rho_C^2}}{\left(\dfrac{\rho_C}{\rho_{A,C}} - 1\right)^2} + \frac{\dfrac{u^2(\rho_{A,M})}{\rho_{A,M}^2} - 2\dfrac{u(\rho_{A,M},\rho_M)}{\rho_{A,M}\rho_M} + \dfrac{u^2(\rho_M)}{\rho_M^2}}{\left(\dfrac{\rho_M}{\rho_{A,M}} - 1\right)^2} \qquad (19.156)$$

3214 Evaluation of this uncertainty requires estimates of ρ_M, ρ_C, $\rho_{A,M}$ and $\rho_{A,C}$ as well as their standard
3215 uncertainties and covariances. The covariance $u(\rho_{A,C},\rho_C)$ is usually zero or negligible, and
3216 $u(\rho_{A,M},\rho_M)$ also is usually negligible if the material being weighed is a solid.

3217 The density of air at any time (ρ_A) depends on temperature, pressure, and humidity, as shown in
3218 the following equation.

$$\rho_A = \rho_0\left(\frac{273.15}{273.15 + T}\right)\left(\frac{P - (0.3783)(\mathrm{RH}/100\%)(P_{\mathrm{Vap}})}{760}\right) \qquad (19.157)$$

3219 where
3220 ρ_A is the density of air
3221 ρ_0 is the density of dry air at 0 °C and 760 torr (mm of Hg)
3222 T is the temperature (°C)
3223 P is the barometric pressure (torr)
3224 RH is the relative humidity (%)
3225 P_{Vap} is the vapor pressure (torr) of water at temperature T

3226 The vapor pressure, P_{Vap}, is a nonlinear function of T, but it can be approximated by a linear
3227 function in the range of temperatures typically encountered in the laboratory. When this approxi-
3228 mation is made, the resulting equation for the air density (g mL^{-1}) may be written as follows.

$$\rho_A = \frac{aP - (\mathrm{RH})(bT - c)}{273.15 + T} \qquad (19.158)$$

3229 where

$a = 4.64746 \times 10^{-4}$

$b = 2.5211151 \times 10^{-6}$

$c = 2.0590571 \times 10^{-5}$

Then the standard uncertainty of ρ_A is given by

$$u(\rho_A) = \frac{\sqrt{a^2 u^2(P) + (b\,\mathrm{RH} + \rho_A)^2 u^2(T) + (bT - c)^2 u^2(\mathrm{RH})}}{273.15 + T} \tag{19.159}$$

The density 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

Suppose the density of the weighed material, ρ_M, is 0.5 g mL^{-1} with a tolerance of 0.2 g mL^{-1}, assumed to represent the half-width of a triangular distribution. The density of the calibration mass standard, ρ_C, is 7.850 g mL^{-1} with a tolerance of 0.025 g mL^{-1}. Instead of measuring temperature, pressure and humidity at the time of each measurement, the laboratory assumes the following nominal values and tolerances:

Temperature	22.5	± 4	°C
Pressure	750	± 20	torr
Relative humidity	50	± 20	%

3249 Then

$$\rho_{A,C} = \rho_{A,M} = \frac{aP - (\mathrm{RH})(bT - c)}{273.15 + T}$$

3250
$$= \frac{(4.64746 \times 10^{-4})(750) - (50)((2.5211151 \times 10^{-6})(22.5) - 2.0590571 \times 10^{-5})}{273.15 + 22.5}$$

$$= 1.1728 \times 10^{-3}\ \mathrm{g\ mL^{-1}}$$

3251 If each of the tolerances for T, P, and RH represents the half-width of a rectangular
3252 distribution, then

3253
$$u^2(T) = \frac{4^2}{3} = \frac{16}{3}, \qquad u^2(P) = \frac{20^2}{3} = \frac{400}{3}, \qquad \text{and} \qquad u^2(\mathrm{RH}) = \frac{20^2}{3} = \frac{400}{3}$$

3254 So, the standard uncertainties of $\rho_{A,C}$ and $\rho_{A,M}$ are

$$u(\rho_{A,C}) = u(\rho_{A,M}) = \frac{\sqrt{a^2 u^2(P) + (b\,\mathrm{RH} + \rho_A)^2 u^2(T) + (bT - c)^2 u^2(\mathrm{RH})}}{273.15 + T}$$

3255
$$= \frac{\sqrt{a^2(400/3) + (b(50) + 1.1728 \times 10^{-3})^2(16/3) + (b(22.5) - c)^2(400/3)}}{273.15 + 22.5}$$

$$= 2.1 \times 10^{-5}\ \mathrm{g\ mL^{-1}}$$

3256 Then the buoyancy correction factor is

3257
$$B = \frac{1 - \rho_{A,C}/\rho_C}{1 - \rho_{A,M}/\rho_M} = \frac{1 - 1.1728 \times 10^{-3}/7.85}{1 - 1.1728 \times 10^{-3}/0.5} = 1.00220$$

3258 The tolerances for the densities ρ_C and ρ_M are the half-widths of triangular distributions; so,

3259
$$u^2(\rho_C) = \frac{0.25^2}{6} \qquad \text{and} \qquad u^2(\rho_M) = \frac{0.2^2}{6}$$

The covariances $u(\rho_{A,C}, \rho_C)$ and $u(\rho_{A,M}, \rho_M)$ are zero in this example. So, the standard uncertainty of B is

$$u(B) = B\sqrt{\frac{u^2(\rho_{A,C})/\rho_{A,C}^2 + u^2(\rho_C)/\rho_C^2}{(\rho_C/\rho_{A,C}-1)^2} + \frac{u^2(\rho_{A,M})/\rho_{A,M}^2 + u^2(\rho_M)/\rho_M^2}{(\rho_M/\rho_{A,M}-1)^2}}$$

$$= 1.00220\sqrt{\frac{\frac{(2.1\times10^{-5})^2}{(1.1728\times10^{-3})^2} + \frac{0.25^2/6}{7.85^2}}{\left(\frac{7.85}{1.1728\times10^{-3}}-1\right)^2} + \frac{\frac{(2.1\times10^{-5})^2}{(1.1728\times10^{-3})^2} + \frac{0.2^2/6}{0.5^2}}{\left(\frac{0.5}{1.1728\times10^{-3}}-1\right)^2}}$$

$$= 3.87\times10^{-4}$$

Thus, the buoyancy correction factor increases the result of the measurement by 0.22% and generates an uncertainty component of approximately 0.04%. Note that this uncertainty component 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.

19G.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

$$u(m) = \sqrt{B^2\left(I^2(\varphi_{Cal}^2 + \varphi_{Env}^2) + \frac{a_L^2}{2} + s_r^2\right) + I^2u^2(B)} \qquad (19.160)$$

where

- m is the buoyancy-corrected mass
- I is the balance indication
- B is the buoyancy correction factor
- φ_{Cal} is the relative standard uncertainty due to calibration
- φ_{Env} is the relative standard uncertainty due to environmental factors
- a_L is the linearity tolerance
- 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 without being removed from the pan. 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 factor for the tare and gross measurements may be different because of the different densities of the container and the material inside it, 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. Finally, the net mass is determined by subtracting the mass of the empty container from the total mass of the container and material. 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

$$m = I_{\text{Net}} B$$
$$u(m) = \sqrt{B^2\left(I_{\text{Net}}^2(\varphi_{\text{Cal}}^2 + \varphi_{\text{Env}}^2) + a_L^2 + 2s_r^2\right) + I_{\text{Net}}^2 u^2(B)} \qquad (19.161)$$

where

I_{Net} is the net balance indication (Gross − Tare)

B is the buoyancy factor for the material being weighed

19G.9 References

American Society for Testing and Materials (ASTM). 1991. *Standard Specification for Laboratory Weights and Precision Mass Standards*, E 617. ASTM, West Conshohocken, PA.

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20 WASTE MANAGEMENT IN A RADIOANALYTICAL LABORATORY

20.1 Introduction

This chapter presents information on the management of radioactive waste generated during analytical processes. Federal, state, and local laws stringently regulate radioactive waste and impose severe consequences for violations. Management of waste in compliance with such regulations is, therefore, critical to the laboratory's sustained operation. Many—but not all—applicable regulations are addressed in this Chapter. A laboratory waste management plan that details procedures for the management of radioactive waste should be implemented before radioactive materials are accepted for processing.

The following sections provide background information on managing radioactive waste and identifies issues that should be considered when preparing a laboratory-waste management plan. Sections 20.2 through 20.5 of this chapter provide general guidance for managing waste in a radioanalytical laboratory. Descriptions of the types of wastes that may be produced in a radioanalytical laboratory are provided in Section 20.2. Section 20.3 reviews various approaches that have been used to achieve effective laboratory-waste management programs. Waste avoidance and waste minimization programs are discussed in Section 20.4. Waste determination and characterization are briefly reviewed in Section 20.5. Some of the specific regulatory requirements that apply to laboratory waste management are provided in Section 20.6. A proposed outline for a waste management plan is provided in Section 20.7, and Section 20.8 suggests a number of useful web resources related to the management of laboratory waste.

20.2 Types of Laboratory Wastes

The types of wastes generated and the waste management issues the laboratory may face are determined by the analytical processes used in the laboratory and the characteristics of the samples analyzed. A laboratory that performs only one or two analytical processes may produce only a few waste streams, whereas a multi-service laboratory that performs a variety of processes may produce many waste streams. Waste streams produced by radioanalytical procedures can include radioactive and non-radioactive wastes. A laboratory waste stream is defined as all wastes that are produced by a given analytical process. Table 20.1 provides a list of wastes that may be generated by a laboratory.

TABLE 20.1 — Examples of Laboratory-Generated Wastes

Waste	Example of Laboratory Generation (Not Inclusive)
Dry solid waste	Gloves, glassware, pipette tips, plastic vials generated through analytical processes
Aqueous waste	Solutions from analytical processes (filtrates, supernates, liquid scintillation fluid)
Organic solvent waste (used solvents, analytical processes)	Used solvents, de-greasers in cleaning operations, liquid scintillation fluid
Acidic wastes	Solutions from analytical processes (filtrates, supernates)
Waste Oil	Used oil from vacuum pumps
Sample	Unused sample from analytical process
Sample residue	Processed sample residue from analytical processes (precipitate, filters, planchets)
Reagent chemicals	Unused, expired, or surplus reagent chemicals
Sanitary waste	Sewage
Sludge waste	Water treatment
Sharps	Analytical processes (gas chromatography)
Various metal wastes/Radioactive sources	Laboratory equipment
Biohazardous waste	Fecal, urine, blood-borne pathogen waste, animal carcasses, body parts, tissues generated from bioassay, tissue or other biological analyses
Toxic Substances Control Act (TSCA) waste	Analytical processes on polychlorinated bi-phenyls (PCB), asbestos, chlorinated dioxin/furans
Radioactive waste	Analytical processes, radioactive standards, radioactive solutions, dry waste, aqueous waste
Resource Conservation and Recovery Act (RCRA) hazardous waste	Analytical processes generating characteristic and listed waste as defined per 40 CFR 261 (Used solvents, reagent chemicals, acidic waste, etc.)
Mixed waste	Analytical processes generating any combination of RCRA waste and radioactive wastes or TSCA waste and radioactive wastes

20.3 Waste Management Program

One source of guidance in assisting the laboratory in developing a waste management plan is *Profile and Management Options for EPA Laboratory Generated Mixed Waste* (EPA, 1996). This report reviews various approaches that have been taken to achieve effective laboratory waste management programs. Much of the EPA report provides a review of articles and books that

detail the experiences of labs that manage radioactive wastes. This section draws significantly from that report.

20.3.1 Program Integration

Successful waste management programs integrate important components, such as administrative, regulatory requirements, training, record keeping, treatment, waste minimization, and prevention. Individual management options, taken in isolation, may not be as effective as a more comprehensive approach to waste management (EPA, 1996). Reviewing all aspects of waste management in the laboratory should reveal the interactions among the component areas, providing insights that allow improvements to the program as a whole without creating unknown negative effects.

20.3.2 Staff Involvement

All levels of management, scientists, and technicians should be actively involved in developing and implementing the waste management program since each brings a valuable and unique perspective to the waste management issue. Upper management must be committed to maintaining a current and effective waste management plan because of the significant costs of waste management and because of the serious civil and criminal penalties associated with noncompliance. Program and project managers bring insight regarding issues, such as returning samples to a site, waste management cost recovery, and data quality objectives. These managers are also familiar with a full range of waste management alternatives. Laboratory environmental, safety, and health personnel are essential to the process since they typically interface with regulators to ensure that waste management practices are fully compliant. The input from laboratory supervisors, scientists, and technicians is necessary because they generate waste at the bench level and have first-hand process knowledge of how various waste streams are produced. These individuals also have to implement the waste management plan on a daily basis and can provide valuable feedback on improving the waste management system.

Waste generation planning is essential to proper waste management. Waste life cycle management is a concept within the U.S. Department of Energy (DOE) Order 435.1 to reduce the amount of radioactive waste generated. Waste life cycle is described as the life of a waste from generation through storage, treatment, transportation, and disposal. For waste generated from a new project or activity, consideration of the waste begins in the planning stage of the project or activity.

20.4 Waste Minimization

Waste avoidance actively reduces the amount of waste to be managed and is a critical part of a waste management plan. An integrated approach to laboratory waste management necessarily implies pollution prevention. The term pollution prevention has served as an all-encompassing term for any technique, process, or procedure that minimizes waste. Broadly defined, pollution prevention refers to activities that keep pollutants from being created in any media (i.e., control pollution at the source). There are many strong benefits to pollution prevention including safety, waste minimization, efficiency, regulatory compliance, reduction in liability, and cost reduction. Pollution prevention techniques are a critical component of prudent laboratory practices and have been incorporated into many laboratory waste management procedures (EPA, 1996).

Management options that address waste avoidance will result in the most substantial cost savings. Two of the primary areas to review when seeking to minimize laboratory waste are the processes and definitions that the laboratory uses to identify and categorize waste. A laboratory may define and manage various categories of wastes and may develop a hierarchy of waste streams similar to the one described in Table 20.1. Properly categorizing waste at the point of production will help to ensure health, safety, and regulatory compliance. This process also will help to avoid unnecessary, costly, and inappropriate treatment, storage, and disposal. However, proper categorization of waste streams can be difficult, requiring knowledge of the chemical and radiological characteristics of the wastes, the production process, and a thorough understanding of all-applicable regulations and regulatory guidance. Waste management regulations were written primarily to regulate industrial production facilities and commercial storage, treatment, and disposal facilities; their application to laboratories may not be readily apparent. The laboratory waste management plan should require that each waste stream be identified prior to production, so that waste minimization steps may be taken and production of unknown wastes avoided.

The processes and definitions that a laboratory uses to determine that a waste is radioactive or non-radioactive have a great influence on the amount of radioactive waste that a laboratory must manage. The regulations offer little or no guidance for establishing that a waste is non-radioactive, therefore it may be up to the laboratory to make this determination. Laboratory management should develop clear guidelines to make this determination. The guidelines must comply with requirements specified by the agency that issues the laboratory's license for radioactive materials since waste considered non-radioactive in one state may be considered radioactive in another.

Once the waste has been properly categorized (either through 10 CFR Part 61 or DOE O 435.1), the laboratory can prioritize the review of waste streams for elimination, reduction, or modification. A waste stream schematic or flow diagram that lists waste stream characteristics and management pathways can be a useful tool in reviewing waste stream management. Various management options that have been used to achieve waste stream minimization include the following:

REGULATORY. Some wastes may be exempted from regulations because of the production process, level of contaminants, volume of waste produced, or management option chosen. For example, some hazardous wastes may be disposed in an industrial wastewater discharge if their contaminants are below established regulatory levels and if the discharge is regulated under the Clean Water Act. Also, a hazardous waste generator that produces less than 100 kg of waste in a month may be considered a conditionally exempt small quantity generator and thus be exempt from many of the requirements of RCRA (40 CFR 261.5). Some radioactive waste may be managed as not-radioactive if the total level of radioactivity is below an exempt or *de minimis* level, or if the activity for specific radionuclides is below established levels (10 CFR 61 20.2005). For certain licensees, radioactive wastes are released into the environment as gaseous and liquid effluents in accordance with 10 CFR Part 61 20.2001(a)(3) and specific license conditions.

METHOD SELECTION. The analytical method selected for the analysis of radioactive material determines the type and volume of waste generated. When two methods will achieve the required measurement quality objectives of the project, the laboratory may select the method that produces the most easily managed waste (see Chapter 6, *Selection and Application of an Analytical Method*).

PRODUCT SUBSTITUTION. In an analytical method, it may be possible to replace a hazardous reagent with a non-hazardous reagent and still meet all health, safety, and data quality objectives. In addition, substituting a short-lived radionuclide for a long-lived radionuclide may ultimately result in a reduction of radioactive waste.

SAMPLE VOLUME COLLECTED. Excess sample material should not be collected. Personnel should only collect enough sample material for the planned analysis and any reserve needed for re-analysis or potential future use. Reserve volume should be minimized with up-front planning.

SAMPLE/REAGENT VOLUME. It may be possible to reduce the amount of sample and/or reagents used in a method. It may also be possible to convert a method to a micro-scale method that uses significantly less sample and reagents than the original method.

REAGENT PROCUREMENT CONTROLS. Often, the quantities of chemicals purchased by a laboratory are determined by the price discounts available on larger quantities, instead of by the amount of chemical required. The real cost of chemicals should be recognized as the initial purchase price plus any disposal costs (lifetime costs). It should be noted that disposal costs of excess chemicals can easily exceed the initial purchase costs. Procurement procedures for hazardous material should be implemented to determine if a non-hazardous substitute is available. Rotating chemical stock (first in, first out) may help avoid expiration of the chemical shelf life.

RE-USE OF MATERIALS. Some materials may be recovered from the analytical process and re-used in subsequent analyses. For example, distillation of certain used organic solvents may purify them sufficiently for reuse.

DECAY IN STORAGE. Since the level of radioactivity decreases with time, it may be possible to store a short-lived radionuclide until the natural-decay process reduces the radioactivity to a level at which the waste can be considered non-radioactive for waste management purposes. Laboratory management should be aware that RCRA storage limitations might impact the feasibility of this option.

WASTE STREAM SEGREGATION. Segregating wastes by the appropriate category allows them to be managed by the most cost-effective option. Combining highly regulated waste streams with less stringently regulated waste streams usually requires the total waste stream to meet the most stringent waste management requirements. For example:

- Non-hazardous waste mixed with hazardous waste must be managed as hazardous waste.
- Non-radioactive waste mixed with radioactive waste must be managed as radioactive waste.
- Hazardous waste mixed with radioactive waste must be managed in compliance with the requirements of the Atomic Energy Act (AEA), RCRA, and TSCA.

20.5 Waste Determinations and Characterization

Laboratory wastes should be properly characterized to assure compliance with applicable federal, state, and local regulations, and to determine appropriate means of disposal. Waste container contents should be adequately characterized during waste generation and packaging. Characterizations should address the type of material and the physical and chemical characteristics of the waste. Minimum waste characterization criteria may be specified for the radioactive waste generated (DOE M 435.1-1, Ch. IV, Sec. I and NRC criteria specified in 10 CFR Part 61 for commercial low-level radioactive waste sites).

Three basic methods of characterization are denoted here: (a) process knowledge; (b) chemical characterization through laboratory analysis; and (c) activities. Factual process knowledge (e.g., from a process waste assessment) influences the amount of sampling required to correctly characterize waste.

A generic laboratory waste management plan should be established to describe the waste life cycle. This plan should focus on characterizing each waste stream and establishing a waste stream profile, so that the waste stream can be properly managed. The profiled waste stream may only require a periodic partial characterization, based on the profile and regulatory status.

20.6 Specific Waste Management Requirements

This section provides general guidance on the storage, treatment, and disposal of radioactive waste generated within a laboratory. It should not be used as definitive guidance for managing radioactive waste. Laboratory managers are encouraged to review the complete regulatory requirements in developing a waste management plan to fit the compliance and operational needs of the laboratory. Laboratory managers may choose to have an environmental compliance specialist assist with developing the waste management plan since waste management requirements can be complex and contradictory.

Radioactive waste is regulated under AEA, administered by the Nuclear Regulatory Commission (NRC). Thirty states are NRC Agreement States and have the authority and the regulatory programs in place to regulate radioactive materials management in accordance with 10 CFR Part 61. Some wastes may also be regulated under RCRA , TSCA, or both, administered by EPA. Most states have been granted authority to administer the mixed waste rules under RCRA. Although many of the state hazardous waste laws are very similar to the federal RCRA regulations, important differences may exist. This chapter focuses only on the federal requirements, therefore, to ensure compliance with all applicable regulations, laboratory management is strongly encouraged to review state and local regulations when developing a waste management plan. Wastes that are regulated as radioactive under AEA and as hazardous under RCRA or TSCA are termed "mixed wastes." Laboratories that generate mixed waste must satisfy both NRC, which regulates the radioactive component, and EPA, which regulates the hazardous component. Mixed waste management is a difficult responsibility, due to the complex regulatory framework and the lack of approved treatment and disposal options for these wastes. Other laws, such as the Clean Water Act (CWA) and the Clean Air Act (CAA), are not summarized in this chapter. However, they may also have some impact on the management of radioactive waste.

Federal regulatory requirements for waste management are found in Title 10 of the *Code of Federal Regulations* (10 CFR) and Title 40 of the *Code of Federal Regulations* (40 CFR). The following Federal citations address specific areas that regulate the management of waste generated by a laboratory.

NRC REQUIREMENTS FOR RADIOACTIVE WASTE. Title 10 CFR 20, *Standards for Protection Against Radiation*, and 10 CFR 61, *Licensing Requirements for Land Disposal of Radioactive Waste*, address issues that may apply to management of radioactive waste in the laboratory.

LICENSE. Each laboratory that handles radioactive materials must be licensed by NRC, a NRC Agreement State, or be operating under a site-wide license held by DOE. Radioactive materials license issued by NRC or an Agreement State may provide additional requirements that affect the management of waste. DOE-owned laboratories might be required to comply with DOE orders that regulate the management of radioactive wastes (such as O 435.1 or 5820.2a).

DOE REQUIREMENTS FOR RADIOACTIVE WASTE. Any generator of DOE radioactive waste and radioactive recyclable materials shall have a Waste Certification Plan (WCP). This plan provides assurance that appropriate sections of the acceptance criteria of the waste and applicable RCRA waste analysis requirements are met (DOE Order 5820.2A, *Radioactive Waste Management*). The radioactive waste generator requirements are to ensure the development, review, approval, and implementation of a program for waste generation planning, characterization, certification, and transfer. This program shall address characterization of waste, preparation of waste for transfer, certification that waste meets the receiving facility's radioactive waste acceptance requirements, and transfer of waste (DOE M 435.1-1).

RCRA REQUIREMENTS FOR HAZARDOUS WASTE. Laboratories that generate hazardous waste must meet detailed and specific requirements for the storage, treatment, and disposal of that waste. Some of the regulatory requirements vary with the total amount of hazardous waste generated each month, thus it is important that the laboratory understand how to properly categorize its operation (small quantity exempt generator, small quantity generator, or large quantity generator). Generator status is a regulatory issue that may vary among states. RCRA regulations for generators found in 40 CFR 260-262, *Hazardous Waste Management System: General*, list requirements in the following sections:

- 40 CFR 261, *Identification and Listing of Hazardous Waste*, describes what is, and what is not, hazardous waste and how to determine if a waste is considered hazardous under RCRA.

- 40 CFR 262, *Standards Applicable to Generators of Hazardous Waste*, establishes management requirements for generators of hazardous waste.

- 40 CFR 262.34, *Accumulation Time*, provides specific time and volume limitations on the storage of hazardous waste.

- 40 CFR 262.40, *Recordkeeping and Reporting*, lists requirements a generator must meet in documenting and reporting hazardous waste management activities.

TSCA REQUIREMENTS FOR PCB WASTE. The primary TSCA regulations that normally would apply to an analytical laboratory relate to PCB waste. Laboratory waste containing PCBs at concentrations of 50 ppm or greater, or are derived from PCB waste samples with concentrations of 50 ppm or greater, are considered PCBs and are subject to the following regulations:

- 40 CFR 761.60, *Disposal Requirements*, describes requirements for the disposal of PCB waste.

- 40 CFR 761.61, *Polychlorinated Biphenyls (PCBs) Manufacturing, Processing, Distribution in Commerce, and Use Prohibitions*, establishes prohibitions of, and requirements for, the manufacture, processing, distribution in commerce, use, disposal, storage, and marking of PCBs and PCB items.

- 40 CFR 761.65, *Storage and Disposal*, describes time limits for storage and storage requirements of PCB waste.

- 40 CFR 761.64, *Disposal of Wastes Generated as a Result of Research and Development Activities ... and Chemical Analysis of PCBs*, provides regulatory exclusion for some PCB analytical samples.

20.6.1 Sample/Waste Exemptions

Laboratory samples and certain mixed wastes may be exempted or excluded from certain regulatory provisions. Management should evaluate those regulations to determine if they affect their waste management practices. Three examples are provided below.

RCRA ANALYTICAL SAMPLE/TREATABILITY SAMPLE EXCLUSIONS. Under 40 CFR 261.4(d), a sample of solid waste or a sample of water, soil, or air, which is collected for the sole purpose of testing to determine its characteristics or composition, is not subject to certain RCRA regulations

if the laboratory is meeting the conditions specified in 40 CFR 261.4. Similarly, samples undergoing treatability studies, and the laboratory or testing facility conducting such treatability studies, are not subject to certain portions of RCRA [40 CFR 261.4(e)]. However, once a material can no longer be considered a sample, it becomes waste and is subject to RCRA requirements.

POLYCHLORINATED BIPHENYL (PCB) SAMPLE EXCLUSION. Portions of samples used in a chemical extraction and analysis method for PCBs, and extracted for purposes of determining the presence of PCBs or concentration of PCBs, are unregulated for PCB disposal (40 CFR 761.64). All other PCB wastes from laboratory operations must be disposed in accordance with 40 CFR 761.61. Radioactive PCB waste may be exempt from the one year time limit for storage if the waste is managed in accordance with all other applicable federal, state, and local laws and regulations for the management of radioactive material (40 CFR 761.65).

MIXED WASTE EXEMPTION. Since August 1991, EPA has maintained a special policy on the enforcement of the storage prohibition of RCRA mixed waste, which applies to generators that are storing mixed wastes for which no viable treatment technology or disposal capacity exists. The policy explains that EPA considers violation of the RCRA storage prohibition in section 3004(j) of RCRA to be a relatively low priority item among the Agency's potential civil enforcement actions, as long as the wastes are stored in accordance with a RCRA permit or interim status or in an environmentally sound manner. This policy, which only applies to certain wastes, has been extended to October 2001. However, the policy does not apply to DOE facilities.

20.6.2 Storage

Regulatory requirements for the storage of radioactive, hazardous, or PCB waste vary by the type of waste, and typically address the waste storage area, type of acceptable waste containers, length of time the waste may be stored, marking the storage area and the containers, and waste monitoring. Significant civil and criminal penalties exist for storing waste improperly or for a longer time period than allowed. The following sections summarize some of these requirements. However, laboratory management is encouraged to review the regulations in depth so they may develop a waste management plan that meets the compliance and operational needs of the laboratory.

In the case of DOE analytical contract laboratories, low-level radioactive waste that has an identified path to disposal shall not be stored longer than one year prior to disposal, except for the purpose of radioactive decay. Low-level waste that does not have an identified path to

disposal shall be characterized as necessary to meet the data quality objectives and minimum characterization requirements to ensure safe storage and to facilitate disposal (DOE M 435.1-1).

20.6.2.1 Container Requirements

RADIOACTIVE WASTE. NRC has container requirements for low-level waste. Refer to 10 CFR Part 61 for Class B and C requirements. For disposal, NRC requires the use of a high integrity container approved by NRC.

RCRA HAZARDOUS WASTE. 40 CFR 265.170-177 provides requirements for the use and management of containers storing hazardous waste. In summary, this section requires that containers be in good condition, be compatible with the waste stored, be closed at all times except when adding or removing waste, and be inspected weekly, in the case of 90-day accumulation areas, for signs of corrosion or leakage.

PCB WASTE. 40 CFR 761.65 details TSCA requirements for the storage of PCB waste, including the physical constraints of the storage area and the type of containers acceptable for storing liquid and non-liquid PCB wastes. Laboratory PCB waste and samples returned to the sample collector or submitted to a disposal facility when sample use is terminated may be exempt from the storage requirements of 40 CFR 761.65.

20.6.2.2 Labeling Requirements

RADIOACTIVE WASTE. Radioactive waste storage areas should be posted with signs and labeled in accordance with 10 CFR 20.1901 -1906, *Precautionary Procedures*. This section specifies requirements for caution signs, labeling, signals, controls, and the storage of licensed material in unrestricted areas.

RCRA HAZARDOUS WASTE. Hazardous waste containers must be labeled with the words "Hazardous Waste" and, in the case of a 90-day accumulation area, the date upon which the waste accumulation began 40 CFR 262.34(a)(4)(c)(ii).

PCB WASTE. 40 CFR 761.40 and 761.45 provides requirements for marking and labeling PCB containers and the PCB storage area (40 CFR 761.50).

20.6.2.3 Time Constraints

RADIOACTIVE WASTE. NRC regulations in Title 10 of the *Code of Federal Regulations* do not specifically establish a maximum amount of time that one may store radioactive waste. A facility's NRC or Agreement State radioactive materials license may address this issue.

RCRA-HAZARDOUS WASTE. A generator may store hazardous waste up to 90 days, 180 days, or 270 days depending on its status as defined by the regulations or the distance the generator is from the disposal facility (40 CFR 262.34). A generator may accumulate as much as 55 gallons of hazardous waste or one quart of acutely hazardous waste in containers at or near the point of generation where wastes initially accumulate, which is under the control of the operator of the process generating the waste (40 CFR 262.34). The storage time clock (90, 180, or 270 days) does not begin until the waste volume reaches 55 gallons (or one quart, in the case of acutely hazardous waste), or whenever waste is stored in a 90-day accumulation area.

PCB WASTE. Radioactive PCB waste may be exempt from the one-year time limit for PCB storage if the waste is managed in accordance with all other applicable federal, state, and local laws and regulations for the management of radioactive material (40 CFR 761.65). According to 40 CFR 761.65(a)10, certain PCB waste containers may be exempt from 40 CFR 761.65 if the containers are disposed within 30 days.

20.6.2.4 Monitoring Requirements

RADIOACTIVE WASTE. Radioactive waste storage areas should be surveyed and personnel should be monitored in accordance with 10 CFR 20.1901-1906, *Precautionary Procedures*. These sections specify the requirements for surveys, personnel monitoring, and storage of licensed material in unrestricted areas. 10 CFR 20.1101 and 10 CFR 20.1201 address permissible doses, levels, and concentrations of airborne radiation that would apply to radioactive waste storage areas.

RCRA HAZARDOUS WASTE. The owner or operator of a hazardous waste storage area must inspect areas in which containers are stored, at least weekly, looking for leaks and deterioration caused by corrosion or other factors (40 CFR 265.174). 40 CFR 262.34 address requirements for Prevention and Preparedness, Contingency Plans, and Emergency Procedures that may apply to a laboratory that stores RCRA waste.

PCB WASTE. All PCB containers in storage shall be checked for leaks at least once every 30 days [40 CFR 761.65(c)(5)].

20.6.3 Treatment

Radioactive and mixed waste may require treatment to meet one or more objectives prior to final disposal. Treatment involves the physical or chemical processes that result in a waste form that is acceptable for disposal or further treatment. Treatment objectives include: (1) producing a waste form acceptable for land disposal; (2) volume/mobility reduction through possible solidification or sizing; (3) producing a waste more amenable for further treatment; or (4) separating radioactive components from RCRA or TSCA components. Another treatment objective is to convert

a radioactive RCRA regulated waste to a radioactive non-RCRA waste. *Special permits may be required from regulatory agencies prior to the treatment of waste.*

Radioactive wastes may require treatment to meet the waste characteristics provided in 10 CFR 61.56. The following types of treatment have been used to meet those requirements:

- Non-solid radioactive waste may be treated with various solidification agents (such as cement, asphalt, or polymers) to immobilize waste or sludge not otherwise acceptable for disposal. Low-level radioactive waste (LLRW) may be absorbed onto a porous material, such as silica, vermiculite, or organic materials to reduce the liquid volume.

- Dry radioactive waste may be treated with compaction or super-compaction to reduce the waste volume.

- Some radioactive waste items may be decontaminated for unrestricted release by removal of surface radioactivity through chemical or physical means. The residue from the decontamination of a surface may require disposal as a radioactive waste.

- The relatively short half-lives of some radionuclides warrant storing the waste for a period of time. Once the levels of radioactivity are undetectable or below an accepted *de minimis* level, the waste may be disposed as a non-radioactive waste or in accordance with license conditions.

20.6.4 Disposal

The disposal of radioactive waste is regulated by NRC in accordance with 10 CFR 20.2001, which requires that waste be disposed at a licensed LLRW site. Radioactive waste that is mixed with waste regulated under RCRA or TSCA is also subject to disposal requirements of the respective regulations. Mixed waste must go to a facility that is licensed under both of the appropriate laws. For example, radioactive RCRA waste cannot go to a RCRA landfill that is not licensed under the Low Level Radioactive Waste Policy Act (LLRWPA), nor can it be disposed at a LLRW site that is not licensed under RCRA.

In some cases, radioactive material may be disposed in a sanitary-sewage system if the requirements of 10 CFR 20.2003 are met. This section provides specific limits on the quantity of radionuclides that can be discharged into a sewage system. Discharges into a sewage system may also be regulated by the Clean Water Act. For example, media used for liquid scintillation counting, containing tritium (^{3}H) or carbon-14 (^{14}C) in concentration of 0.05 microcuries per gram or less may be disposed as if it were not radioactive. Also, animal tissue containing ^{3}H or ^{14}C at levels less than or equal to 0.05 microcuries per gram (1,850 Bq/g) may be disposed without regard to radioactivity (10 CFR 20.2005).

The DOE also regulates the disposal of radioactive waste. Under DOE M 435.1-1, all radioactive waste generators must have a waste certification program to ensure that the waste acceptance criteria for the radioactive disposal facility are met. An outline of a waste certification plan is contained in the following section.

20.7 Contents of a Laboratory Waste Management Plan/Certification Plan

20.7.1 Laboratory Waste Management Plan

A laboratory waste management plan will describe the waste generated by the analytical laboratory. Each section of the plan is usually divided into two separate entities B one addressing the needs of the laboratory analyst and the second addressing the needs of the waste management personnel. An outline of a generic plan follows:

1. Recyclable Wastes
2. Sanitary Wastes/Industrial Wastes
3. Radioactive Wastes
4. Hazardous and Mixed Wastes
   - Satellite Accumulation Area operations
   - 90-day Accumulation Area operations

Within each section, the laboratory should delineate the types of waste that fall into each category. Also, within the section for laboratory analysts, the disposal of the waste should be clearly defined (e.g., paper in recyclable waste bin, unknown waste to environmental and/or waste personnel). The waste management section should describe the process used by the waste management personnel to dispose of the waste.

20.7.2 Waste Certification Plan/Program

The general outline for waste certification plans described below was taken from DOE M 435.1-1 Ch. IV, Sec. J (1-3):

CERTIFICATION REQUIREMENTS. The waste certification program shall designate the officials who have the authority to certify and release waste for shipment and to specify the documentation required for waste generation, characterization, shipment, and certification. The program shall provide requirements for auditing, retrieving and storing required documentation, including records retention.

CERTIFICATION BEFORE TRANSFER. Low-level waste shall be certified as meeting waste acceptance requirements before it is transferred to the facility receiving the waste.

MAINTAINING CERTIFICATION. Low-level waste that has been certified as meeting the waste acceptance requirements for transfer to a storage, treatment, or disposal facility shall be managed in a manner that maintains its certification status.

A general outline for a laboratory waste certification plan follows:

1. FACILITY NAME AND LOCATION. Provide the name and the physical location of the facility.

2. ORGANIZATION. Describe the organizational structure for the facility's operation, quality assurance program, and waste management program.

3. CONTENTS OF WASTE CERTIFICATION PLAN. Provide a detailed Table of Contents, including list of tables, figures, and appendices as appropriate.

4. FACILITY RECYCLABLE AND WASTE MINIMIZATION STRATEGY. Identify the wastes and waste streams the facility has targeted for recycling and waste minimization (i.e., source reduction through product replacement).

5. DUTIES AND RESPONSIBILITIES OF MANAGEMENT AND WASTE MANAGEMENT PERSONNEL. Provide a description of the positions at the laboratory, including primary and secondary responsibilities and line of reporting.

6. QUALIFICATION REQUIREMENTS AND TRAINING OF WASTE MANAGEMENT PERSONNEL. Describe the training and qualification program implemented for the environmental and waste personnel. No specialized certifications (e.g., certified hazardous materials manager, professional engineer) is needed unless specified by the job description or standard operation procedures.

7. QUALIFICATIONS OF PROCEDURES AND EQUIPMENT USED IN WASTE MANAGEMENT. Describe all equipment used in the waste management processes and procedures.

8. RECYCLABLE MATERIAL AND WASTE SEGREGATION CONTROL. Describe the process of segregating various types of waste streams, especially in regards to radioactive and non-radioactive wastes.

9. PACKAGING, HANDLING AND STORAGE CONTROL. Describe the process of packaging, handling, and storing waste at the facility. This would include drum inspections, cipher-locked storage, etc. The disposal of the supernates is a third example of a waste stream. These supernates may be disposed in a sewage system, but the pH must be above 2 or below 12 to allow the supernate solutions to be exempt from RCRA regulations. Elementary neutralization is allowed in the laboratory under RCRA, but state regulations

may require registration of the laboratory as an elementary neutralization unit before neutralization and disposal take place.

20.8 Useful Web Sites

Listed below are useful federal web sites relevant to the management of laboratory waste. Due to the nature of the Internet, these addresses may change in the future.

Federal and State Government Regulation and Program References
http://www.epa.gov/docs/epacfr40/find-aid.info/state/

Environmental Laws and Regulations, Full Text (U.S. Code)
More than a dozen major statutes or laws form the legal basis for the programs of the Environmental Protection Agency (EPA). The full text of these laws and the U.S. Code Citation for each environmental law can be accessed through the following address.
http://www.epa.gov/epahome/lawreg.htm

Environmental Regulations in *Federal Register*
Full text of all *Federal Register* documents issued by EPA, as well as selected documents issued by other Departments and Agencies. Notices, meetings, proposed rules, and regulations are divided into twelve topical categories for easy access (e.g., air, water, pesticides, toxics, and waste).
http://www.epa.gov/fedrgstr/

State and Federal Agency Contact List for Mixed Waste Regulations
http://www.epa.gov/rpdweb00/mixed-waste/mw_pg6e.htm

States and Territories Where EPA Regulates Mixed Waste
http://www.epa.gov/rpdweb00/mixed-waste/mw_pg6a.htm

States and Territories With EPA Authorization to Regulate Mixed Waste
http://www.epa.gov/rpdweb00/mixed-waste/mw_pg6b.htm

State Solid and Hazardous Waste Web Sites
http://www.epa.gov/epaoswer/osw/stateweb.htm

RCRA State Authorization, By State and Program Element
http://www.epa.gov/epaoswer/hazwaste/state/index.htm

NRC Agreement States
http://www.hsrd.ornl.gov/nrc/asframe.htm

DOE Mixed Waste Policies
http://www.directives.doe.gov/

EPA Mixed Waste Home Page
http://www.epa.gov/rpdweb00/mixed-waste/index.html

Mixed Waste Glossary
http://www.epa.gov/radiation/mixed-waste/mw_pg5.htm#AEA

Guidance on the Definition and Identification of Commercial Mixed Low Level Radioactive and Hazardous Waste
http://www.epa.gov/rpdweb00/mixed-waste/mw_pg25.htm

Current Mixed Waste Treatment, Storage, or Disposal Facilities (TSDFs)
http://www.epa.gov/rpdweb00/mixed-waste/mw_pg11a.htm

NRC/EPA Draft Storage Guidance
http://www.epa.gov/radiation/mixed-waste/mw_pg27.htm

Mixed Waste Shipping and Transportation
http://www.epa.gov/rpdweb00/mixed-waste/mw_pg10.htm

Mixed Waste Pollution Prevention
http://www.epa.gov/rpdweb00/mixed-waste/mw_pg23.htm

Pollution Prevention, EPA Home Page
http://www.epa.gov/epahome/p2pgram.htm

Radioactive Waste Disposal
http://www.nrc.gov/NRC/radwaste.htm

20.9 References

20.9.1 Cited References

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20.9.2 Other Sources

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APPENDIX A: DIRECTED PLANNING APPROACHES

A.1 Directed Planning Approaches

There are a number of approaches being used for directed planning of environmental operations. Some of these approaches were designed specifically for data collection activities; others are applications of more general planning philosophies. Many variations to these approaches have been made for specific applications. The following are some of the approaches being used:

- Data Quality Objectives (DQO);
- Observational Approach (OA);
- Streamlined Approach for Environmental Restoration (SAFER);
- Technical Project Planning (TPP);
- Expedited Site Characterization (ESC);
- Value Engineering;
- Systems Engineering;
- Total Quality Management (TQM); and
- Partnering.

Employing any of these approaches assures that sufficient planning is carried out to define a problem adequately, determine its importance, and develop an approach to solutions prior to spending resources.

This appendix discusses some elements that are common to direct planning processes (Section A.2) and provides in Sections A.3 through A.11 very brief descriptions of the planning approaches listed above. References are listed at the end of the appendix on each of the approaches to provide sources of more detailed information.

Several directed planning approaches have been implemented by the Federal sector for environmental data collection activities. Project planners should be cognizant of agency requirements for planning. MARLAP does not endorse any one planning approach. Users of this manual are encouraged to consider all the available approaches and choose a directed planning process that is appropriate to their project and agency.

A.2 Elements Common to Directed Planning Approaches

To achieve the outcomes desired from directed planning, all of these approaches address the following essential elements:

1. *Defining the problem or need*: Identifying the problem(s) facing the stakeholder/customer that requires attention, or the concern that requires streamlining.

2. *Establishing the optimum result*: Defining the decision, response, product, or result that will address the problem or concern and satisfy the stakeholder/customer.

3. *Defining the strategy and determining the quality of the solution*: Laying out a decision rule or framework, roadmap, or wiring diagram to get from the problem or concern to the desired decision or product and defining the quality of the decision, response, product, or result that will be acceptable to the stakeholder/customer by establishing specific, quantitative, and qualitative performance measures (e.g., acceptable error in decisions, defects in product, false positive responses).

4. *Optimizing the design*: Determining what is the optimum, cost-effective way to reach the decision or create the product while satisfying the desired quality of the decision or product.

To most problem solvers, these four elements stem from the basic tenets of the scientific method: "Principles and procedures for the systematic pursuit of knowledge involving the recognition and formulation of a problem, the collection of data through observation and experiment, and the formulation and testing of hypotheses" (Webster's Dictionary).

Each approach requires that a team of customers, stakeholders, and decision makers defines the problem or concern; a team of technical staff or line operators have the specific knowledge and expertise to define and then provide the desired product; and both groups work together to understand each other's needs and requirements and to agree on the product to be produced. The approaches represent slightly different creative efforts in the problem-solving process. All are intended to facilitate the achievement of optimum results at the lowest cost, generally using team work and effective communication to succeed.

A.3 Data Quality Objectives Process

The Data Quality Objectives (DQO) process was created by the U. S. Environmental Protection Agency's Quality Assurance Management Staff (QAMS) to promote effective communications between decision makers, technical staff, and stakeholders on defining and planning the remediation of environmental problems.

The DQO process consists of seven basic steps:

1. State the problem
2. Identify the decision
3. Identify inputs to the decision
4. Define the study boundaries
5. Develop a decision rule
6. Specify limits on decision errors
7. Optimize the design

Applying the DQO steps requires effective communication between the parties who have the problem and the parties who must provide the solution. Additional information about the DQO Process is provided in Appendix B to this manual.

A.4 Observational Approach

The Observational Approach (OA) emphasizes determining what to do next by evaluating existing information and iterating between collecting new data and taking further action. The name "observational approach" is derived from observing parameters during implementation. OA was developed by Karl Terzaghi (Peck, 1969) for geological applications. In mining operations, there may be substantial uncertainty in the location of valuable geological formations. Information on soil and mineral composition would help to identify such formations. Application of OA utilizes the sampling information on soil and mineral composition to direct the digging locations. OA should be encouraged in situations where uncertainty is large, the vision of what is expected or required is poor, and the cost of obtaining more certainty is very high.

The philosophy of OA when applied to waste site remediation is that remedial action can be initiated without fully characterizing the nature and extent of contamination. The approach provides a logical decision framework through which planning, design, and implementation of remedial actions can proceed with increased confidence. OA incorporates the concepts of data sufficiency, identification of reasonable deviations, preparation of contingency plans, observation of the systems for deviations, and implementation of the contingency plans. Determinations of performance measures and the quality of new data are done as the steps are implemented.

The iterative steps of site characterization, developing and refining a site conceptual model, and identifying uncertainties in the conceptual model are similar to traditional approaches. The concept of addressing uncertainties as reasonable deviations is unique to OA and offers a qualitative description of data sufficiency for proceeding with site remediation.

A.5 Streamlined Approach for Environmental Restoration

The Streamlined Approach for Environmental Restoration (SAFER) is an integration of the DQO process and OA developed by the U. S. Department of Energy (DOE). The planning and assessment steps of SAFER are the DQO process. The implementation steps of SAFER are the Observational Approach. The approach emphasizing team work between decision makers and technical staff reduces uncertainty with new data collection and manages remaining uncertainty with contingency plans. The labels in each SAFER step are slightly different from the DQO and OA steps, but the basic logic is the same. The SAFER Planning steps are:

- Develop a conceptual model;
- Develop remedial objectives and general response actions;
- Identify priority problem(s);
- Identify reasonable deviations and possible contingencies;
- Pursue limited field studies to focus and expedite scoping;
- Develop the decision rule;
- Establish acceptable conditions and acceptable uncertainty for achieving objective; and
- Design the work plan.

A.6 Technical Project Planning

Technical Project Planning (TPP) (formerly Data Quality Design), developed by the U. S. Army Corps of Engineers, is intended for developing data collection programs and defining data quality objectives for hazardous, toxic, and radioactive waste sites (HTRW). This systematic process (USACE, 1998) entails a four-phase planning approach in which a planning team—comprised of decision makers, data users, and data providers—identifies the data needed to support specific project decisions and develops a data collection program to obtain those data. In Phase I, an overall site strategy and a detailed project strategy are identified. The data user's data needs, including the level of acceptable data quality, are defined in Phase II. Phase III entails activities to develop sampling and analysis options for the data needed. During phase IV, the TPP team finalizes a data collection program that best meets the decision makers' short- and long-term needs within all project and site constraints. The technical personnel complete Phase IV by preparing detailed project objectives and data quality objectives, finalizing the scope of work, and preparing a detailed cost estimate for the data collection program. The TPP process uses a multi-disciplinary team of decision makers, data users, and data implementors focused on site closeout.

A.7 Expedited Site Characterization

Expedited Site Characterization (ESC) was developed to support DOE's Office of Science and Technology's Characterization, Monitoring, and Sensor Technology (CMST) program (Burton, 1993). The ESC process has been developed by American Society for Testing and Materials (ASTM) as a provisional standard for rapid field-based characterization of soil and groundwater (ASTM, 1996). The process is also known as QUICKSITE and "expedited site conversion." ESC is based on a core multi-disciplinary team of scientists participating throughout the processes of planning, field implementation, data integration, and report writing. ESC requires clearly defined objectives and data quality requirements that satisfy the needs of the ESC client, the regulatory authority, and the stakeholders. The technical team uses real-time field techniques, including sophisticated geophysical and environmental sampling methods and an on-site analytical laboratory, to collect environmental information. Onsite computer support allows the expert team to analyze data each day and decide where to focus data collection the next day. Within a framework of an approved dynamic work plan, ESC relies on the judgment of the technical team as the primary means for selecting the type and location of measurements and samples throughout the ESC process. The technical team uses on-site data reduction, integration and interpretation, and on-site decision making to optimize the field investigations.

Traditional site investigations generally are based on a phased engineering approach that collects samples based on a pre-specified grid pattern and does not provide the framework for making changes in direction in the field. A dynamic work plan (Robatt, 1997; Robatt et al., 1998) relies—in part—on an adaptive sampling and analysis program. Rather than specify the sample analyses to be performed, the number of samples to be collected and the location of each sample, dynamic work plans specify the decision making logic that will be used in the field to determine where the samples will be collected, when the sampling will stop, and what analyses will be performed. Adaptive sampling and analysis programs change or adapt based on the analytical results produced in the field (Robatt, 1998; Johnson, 1993a,b).

A.8 Value Engineering

Value methodology was developed by Lawrence D. Miles in the late 1940s. He used a function-based process ("functional analysis") to produce goods with greater production and operational efficiency. Value methodology has evolved and, depending on the specific application, is often referred to as "value engineering," "value analysis," "value planning," or "value management." In the mid-1960s value engineering was adopted by three Federal organizations: the Navy Bureau of Shipyards and Docks, the U. S. Army Corp of Engineers, and the U. S. Bureau of Reclamation. In the 1990s, Public Law 104-106 (1996) and OMB Circulars A-131 (1993) and A-11

(1997) set out the requirements for the use of value engineering, as appropriate, to reduce nonessential procurement and program costs.

Value Engineering is a systematic and organized decision-making process to eliminate, without impairing essential functions, anything that increases acquisition, operation, or support costs. The techniques used analyze the functions of the program, project, system, equipment, facilities, services, or supplies to determine "best value," or the best relationship between worth and cost.

The method generates, examines, and refines creative alternatives that would produce a product or a process that consistently performs the required basic function at the lowest life-cycle cost and is consistent with required performance, reliability, quality, and safety.

A standard job plan is used to guide the process. The six phases of the value engineering job plan are:

- Information;
- Speculation (or creative);
- Evaluation (or analysis);
- Evolution (or development);
- Presentation (or reporting); and
- Implementation (or execution).

Value engineering can be used alone or with other management tools, such as TQM and Integrated Product and Process Development (IPPD).

A.9 Systems Engineering

Systems Engineering brings together a group of multi-disciplinary team members in a structured analysis of project needs, system requirements and specifications, and a least-cost strategy for obtaining the desired results. Systems engineering is a logical sequence of activities and decisions that transforms an operational need into a preferred system configuration and a description of system performance parameters. Problem and success criteria are defined through requirements analysis, functional analysis, and systems analysis and control. Alternative solutions, evaluation of alternatives, selection of the best life-cycle balanced solution, and the description of the solution through the design package are accomplished through synthesis and systems analysis and control.

The systems engineering process involves iterative application of a series of steps:

- Mission analysis or requirements understanding;
- Functional analysis and allocation;
- Requirements analysis;
- Synthesis; and
- System analysis and control.

A.10 Total Quality Management

Total Quality Management (TQM) is a customer-based management philosophy for continuously improving the quality of products (or how work is performed) in order to meet customer expectations of quality and to measure and produce results aligned with strategic objectives. TQM grew out of two systems developed by Walter Shewhart of Bell Laboratories in the 1920s. Statistical process control was used to measure variance in production systems and to monitor consistency and diagnose problems in work processes. The "Plan-Do-Check-Act" cycle applied a systematic approach to improving work processes. The work of Deming and others in Japan following World War II expanded the quality philosophy beyond production and inspection to all functions within an organization and defined quality as "fit for customer use."

TQM has been defined as "the application of quantitative methods and the knowledge of people to assess and improve (a) materials and services supplied to the organizations, (b) all significant processes within the organization, and (c) meeting the needs of the end-user, now and in the future" (Houston and Dockstader, 1997). The goal of TQM is to enhance effectiveness of providing services or products. This is achieved through an objective, disciplined approach to making changes in processes that affect performance. Process improvement focuses on preventing problems rather than fixing them after they occur. TQM involves everyone in an organization in controlling and continuously improving how work is done.

A.11 Partnering

Partnering is intended to bring together parties that ordinarily might have differing or competing interests to create a synergistic effect on an outcome each views as desirable. Partnering is a team building and relationship enhancing technique that seeks to identify and communicate the needs, expectations, and strengths of the participants. Partnering combines the talents of the participating organizations in order to develop actions that promote their common goals and objectives. In the synergistic environment of partnering, creative solutions to problems can be developed. Like TQM, partnering enfranchises all stakeholders (team members) in the decision process and holds them accountable for the end results. Each team member (customer, management, employee) agrees to share the risks and benefits associated with the enterprise. Like the

other approaches, partnering places a premium on open and clear communication among stakeholders to define the problem and the solution, and to decide upon a course of action.

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APPENDIX B: THE DATA QUALITY OBJECTIVES PROCESS

B1.0 Introduction

MARLAP's objective in this appendix is to provide information about the basic framework of the DQO process (ASTM 5792; EPA, 2000; NRC, 1998; MARSSIM, 1997). The DQO planning process empowers both data users and data suppliers to take control and resolve issues in a stepwise fashion. It brings together at the right time all key players from the data user and data supplier constituencies and enables each participant to play a constructive role in clearly defining:

- The problem that requires resolution;
- What type, quantity, and quality of data the decision maker needs to resolve that problem;
- Why the decision maker needs that type and quality of data;
- How much risk of making a wrong decision is acceptable; and
- How the decision maker will use the data to make a defensible decision.

The DQO Process provides a logic for setting well-defined, achievable objectives and developing a cost-effective, technically sound sampling and analysis design. It balances the data user's tolerance for uncertainty with the available resources for obtaining data. The number of visible and successful applications of the DQO process has proven its value to the environmental community. The DQO process is adaptable depending on the complexity of the project and the input from the decision makers. Some users have combined DQO planning with remedy selection for restoration projects (e.g., DOE's SAFER—see Appendix A.5). Other users have integrated the project scoping meetings with the DQO Process. Much of the information that is developed during the DQO process is useful for the development of the project plan documents (Chapter 4) and the implementation of the data validation process (Chapter 8) and the data quality assessment (DQA) process (Chapter 9).

Since its inception, the term "data quality objectives" has been adopted by many organizations, and the definition has been adapted and modified (ee box on next page). Throughout this document, MARLAP uses EPA's (2000) definition of DQOs: "Qualitative and quantitative statements derived from the DQO process that clarify study objectives, define the appropriate type of data, and specify the tolerable levels of potential decision errors that will be used as the basis for establishing the quality and quantity of data needed to support decisions."

Definitions of Data Quality Objectives

(1) Statements on the level of uncertainty that a decision maker is willing to accept in the results derived from environmental data (ASTM 5283; EPA, 1986).

(2) Qualitative and quantitative statements derived from the DQO process that clarify study objectives, define the appropriate type of data, and specify the tolerable levels of potential decision errors that will be used as the basis for establishing the quality and quantity of data needed to support decisions (EPA, 2000).

(3) Qualitative and quantitative statements derived from the DQO process describing the decision rules and the uncertainties of the decision(s) within the context of the problem(s) (ASTM D5792).

(4) The qualitative and quantitative statements that specify the quality of the data required to support decisions for any process requiring radiochemical analysis (radioassay) (ANSI 42.23).

B2.0 Overview of the DQO Process

The DQO process (Figure B1) consists of seven steps (EPA, 2000). In general, the first four steps of the DQO Process require the project planning team to define the problem and qualitatively determine required data quality. Once these steps have been addressed adequately, the last three steps of the process establish quantitative performance measures for the decision and the data. The last step of the process involves developing the data collection design based on the DQOs, which is dependent on a clear understanding of the first six steps.

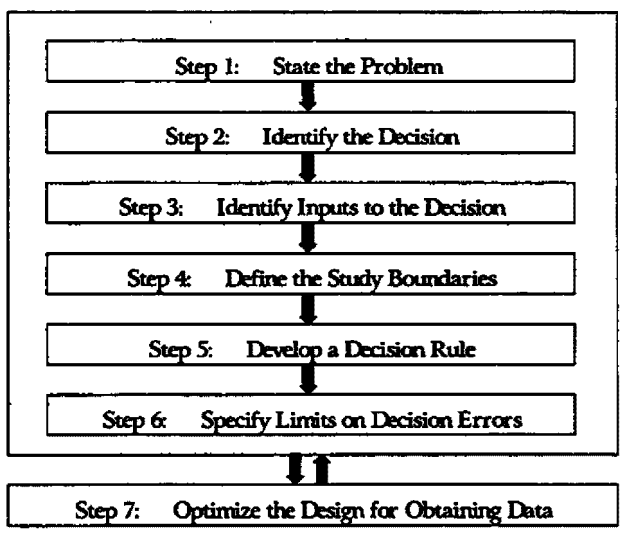

Figure B1—Seven steps of the DQO process.

Although the DQO process is described as a sequence of steps, it is inherently iterative. The output from each step influences the choices that will be made in subsequent steps. For instance, a decision rule cannot be created without first knowing the problem and desired decision. Similarly, optimization of the sampling and analysis design generally cannot occur unless it is clear what is being optimized —the results of the preceding steps. Often the outputs of one step will trigger the need to

rethink or address issues that were not evaluated thoroughly in prior steps. These iterations lead to a more focused sampling and analysis design for resolving the defined problem. The first six steps should be completed before the sampling and analysis design is developed, and every step should be completed before data collection begins. The DQO process is considered complete with the approval of an optimal design for sampling and analysis to support a decision or when available historical data are sufficient to support a decision.

In practice, project planning teams often do a cursory job on the first four steps, wanting to get into technical design issues immediately. Without carefully defining the problem and the desired result, the project planning team may develop a design that is technically sound but answers the wrong question, or answers the questions only after the collection of significant quantities of unnecessary data. Time spent on the first four steps is time well spent. Extra effort must be given to assure that Steps 1 to 4 are adequately addressed.

When applying the DQO process, or any planning approach, it is important to document the outputs of each step to assure that all participants understand and approve the interim products, and that they have a clear record of their progress. It is sometimes useful to circulate an approval copy with signature page to ensure agreement of the stakeholders.

B3.0 The Seven Steps of the DQO Process

Each step of the DQO process will be discussed in the following sections. Not all items will be applicable to every project. The project planning team should apply the concepts that are appropriate to the problem.

B3.1 DQO Process Step 1: State the Problem

The first step is to define the problem clearly. The members of the project planning team present their concerns, identify regulatory issues and threshold levels, and review the site history. The project planning team should develop a concise description of the problem. Some elements to include in the description might be the study objectives, regulatory context, groups who have an interest in the study, funding and other resources available, previous study results, and any obvious sampling design constraints. The more facts, perceptions and concerns of the key stakeholders—including important social, economic, or political issues—that are identified during this step, the better the chances are that the issues driving the decisions and actions will be identified.

The primary decision maker should be identified. The resources and relevant deadlines to address the problem are also defined at this time. If possible, a "site conceptual model" should be developed. This will help structure and package the diverse facts into an understandable picture of what the various issues are and how those issues can be focused into a specific problem. The expected outputs of Step 1 are:

- A conceptual model that packages all the existing information into an understandable picture of the problem;
- A list of the project planning team members and identification of the decision maker;
- A concise description of the problem; and
- A summary of available resources and relevant deadlines for the study.

B3.2 DQO Process Step 2: Identify the Decision

During Step 2 of the DQO Process, the project planning team defines what decision must be made or what question the project will attempt to resolve. The decision (or question) could be simple, like whether a particular discharge is or is not in compliance, or the decision could be complex, such as determining if observed adverse health is being caused by a non-point source discharge. Linking the problem and the decision focuses the project planning team on seeking only that information essential for decision making, saving valuable resources (time and money).

The result may be a comprehensive decision for a straightforward problem, or a sequence of decisions for a complex problem. For complex problems with multiple concerns, these concerns should be prioritized in order of importance. Often a complex concern is associated with a series of decisions that need to be made. Once these decisions have been identified, they should be sequenced in a logical order so the answer to one decision provides input in answering the next decision. It may be helpful to develop a logic flow diagram (decision framework), arraying each element of the issue in its proper sequence along with its associated decision that requires an answer.

The term "action level" is used in this document to denote the numerical value that will cause the decision maker to choose one of the alternative actions. The action level may be a derived concentration guideline level, 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. The release criterion typically is 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. A radionuclide-specific predicted concentration or surface area concentration of specific nuclides that can result in a dose (TEDE or CEDE) or specific risk equal to the release criterion is called the "derived concentration guideline level" (DCGL). A direct comparison can be made between the project's analytical measurements and the DCGL (MARSSIM, 1997).

The project planning team should define the possible actions that may be taken to solve the problem. Consideration should be given to the option of taking no action. A decision statement can then be developed by combining the decisions and the alternative actions. The decision rule and the related hypothesis test will be more fully developed in the DQO process at Steps 5 and 6.

By defining the problem and its associated decision clearly, the project planning team has also begun to define the inputs and boundaries (DQO process Steps 3 and 4). At the end of Step 2, the project planning team has:

- Identified the principal decisions or questions;
- Defined alternative actions that could be taken to solve the problem based on possible answers to the principal decisions and questions;
- Combined the principal decisions and questions and the alternative actions into decision statements that expresses a choice among alternative actions; and
- Organized multiple decisions.

B3.3 DQO Process Step 3: Identify Inputs to the Decision

During Step 3, the project planning team makes a formal list of the specific information required for decision making. The project planning team should determine what information is needed and how it can be acquired. The project planning team should specify if new measurements are required for the listed data requirements. The data required are based on outcomes of discussion during the previous two steps. The project planning team should define the basis for setting the action level. Depending on the level of detail of the discussion during the previous steps, then efforts associated with Step 3 may be primarily to capture that information. If the first two steps have not defined the inputs with enough specificity, then those inputs should be defined here.

However, before going further, the output should be reviewed to assure that the problem, the decision steps and the input are compatible in complete agreement.

An important activity during Step 3 is to determine if the existing data or information, when compared with the desired information, has significant gaps. If no gaps exist, then the existing data or information may be sufficient to resolve the problem and make the decision. (Although there may be no gaps in the data, the data may not have enough statistical power to resolve the action level. See Step 6 for more discussion.) In order to optimize the use of resources, the project planning team should maximize the use of historical information. If new data are required, then this step establishes what new data (inputs) are needed. The specific environmental variable or characteristic to be measured should be identified. The DQO Process clearly links sampling and analysis efforts to an action and a decision. This linkage allows the project planning team to determine when enough data have been collected.

If the project planning team determines that collection of additional data is needed, the analytical laboratory acquisition strategy options should be considered at this stage. Identifying suitable contracting options should be based on the scope, schedule, and budget of the project, and the capability and availability of laboratory resources during the life of the project, and other technical considerations of the project. If an ongoing contract with a laboratory is in place, it is advisable to involve them with the radioanalytical specialists as early as possible.

The project planning team should ensure that there are analytical protocols available to provide acceptable measurements. If analytical methods do not exist, the project planning team will need to consider the resources needed to develop a new method, reconsider the approach for providing input data, or perhaps reformulate the decision statement.

The expected outputs of Step 3 are:

- A list of information needed for decision making;
- Determination of whether data exists and are sufficient to resolve the problem;
- Determination of what new data, if any, are required;
- Defined the characteristics that define the population and domain of interest;
- Defined the basis for the action level;
- Confirmation that appropriate analytical protocols exist to provide the necessary data; and
- A review of the planning output to assure the problem, decision and inputs are fully linked.

B3.4 DQO Process Step 4: Define the Study Boundaries

In Step 4, the project planning team should define clearly the geographic area within which the decisions will apply. The project planning team specifies the spatial and temporal boundaries covered by the decision statement. The spatial boundaries define the physical aspects to be studied in terms of geographic area, media, and any appropriate subpopulations (e.g., an entire plant, entire river basin, one discharge, metropolitan air, emissions from a power plant). When appropriate, divide the population into strata that have relatively homogeneous characteristics. 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). Changing conditions that could impact the success of sampling and analysis and interpretation need to be considered. These factors include weather, temperature, humidity, or amount of sunlight and wind.

The scale of decision is also defined during this step. 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. During Step 4, the project planning team also should identify practical constraints on sampling and analysis that could interfere with full implementation of the data collection design. These include time, personnel, equipment, and seasonal or meteorological conditions when sampling is not possible or may bias the data.

In practice, the study boundaries are discussed when the decision makers agree on the problem and its associated decision. For instance, a land area that may be contaminated or a collection of waste containers would be identified as part of the problem and decision definition in Steps 1 and 2. The boundaries also would be considered when determining inputs to the decision in Step 3. If the study boundaries had not been addressed before Step 4 or if new issues were raised during Step 4, then Steps 1, 2, and 3 should be revisited to determine how Step 4 results are now influencing the three previous steps.

The outputs of Step 4 are:

- A detailed description of the spatial and temporal boundaries of the problem; and
- Any practical constraints that may interfere with the sampling and analysis activities.

B3.5 Outputs of DQO Process Steps 1 to 4 Lead Into Steps 5 to 7

At this stage in the DQO process, the project planning team has defined with a substantial degree of detail the problem, its associated decision, and the inputs and boundaries for addressing that problem. The project planning team knows whether it needs new data to fill specific gaps and what that data should be. The remaining three steps are highly technical and lead to the selection of the sampling and analysis design. Even when new data is not required (i.e., a data collection design is not needed), the project planning team should continue with Steps 5 and 6 of the DQO Process. By establishing the formal decision rule and the quantitative estimates of tolerable decision error rates, the project planning team is assured that consensus has been reached on the actions to be taken and information to establish criteria for DQA process.

It is important to emphasize that every effort must be made to assure that Steps 1 to 4 are adequately addressed. If the necessary time is taken in addressing carefully the first four steps and assuring consensus among the project planning team, then the three remaining steps are less difficult.

B3.6 DQO Process Step 5: Develop a Decision Rule

In Step 5, the project planning team determines the appropriate statistical parameter that characterizes the population, specifies the action level, and integrates previous DQO process outputs into a single "if ..., then ..." statement (called a "decision rule") that describes a logical basis for choosing among alternative actions. (The statistical parameters are discussed in more detail in Chapter 19, *Measurement Statistics.*)

The four main elements to the decision rule are:

1. THE PARAMETER OF INTEREST. A descriptive measure (e.g., mean, median, or proportion) that specifies the characteristic or attribute that the decision maker would like to know and that the data will estimate. The characteristics that define the population and domain of interest was established in Step 3.

2. THE SCALE OF DECISION MAKING. The smallest, most appropriate subset for which decisions will be made. The scale of decision making was previously defined in Step 4.

3. THE ACTION LEVEL. A threshold value of the parameter of interest that provides the criterion for choosing among alternatives. Action levels may be based on regulatory standards or they

may be derived from site- and analyte-specific criteria such as dose or risk analysis. The basis for the action level was determined in Step 3.

4. THE ALTERNATIVE ACTIONS. The actions the decision maker would take, depending on the "true value" of the parameter of interest. The alternative actions were determined in Step 2.

The decision rule is a logical, sequential set of steps to be taken to resolve the problem. For example, "If one or more conditions exits then take action 1, otherwise take action 2."

The outputs of Step 5 are:

- The action level;
- The statistical parameter of interest; and
- An "if ..., then ..." statement that defines the conditions that would cause the decision maker to choose among alternative courses of action.

B3.7 DQO Process Step 6: Specify the Limits on Decision Errors

In Step 6 of the DQO process, the project planning team assesses the potential consequences of making a wrong decision and establishes a tolerable level for making a decision error. The project planning team defines the types of decision errors (Type I and II) and the tolerable limits on the decision error rates. In general, a Type I error is deciding against the default assumption (the null hypothesis) when it is actually true; a Type II error is not deciding against the null hypothesis when it is actually false (see Attachment B1 and Appendix C for detailed discussions). The limits on the decision errors will be used to establish measurement performance criteria for the data collection design.

Traditionally, the principles of statistical hypothesis testing (see Chapter 19) have been used to determine tolerable levels of decision error rates. Other approaches applying decision theory have been applied (Bottrell, et al., 1996a,b). Based on an understanding of the possible consequences of making a wrong decision in taking alternative actions, the project planning team chooses the null hypotheses and judges what decision error rates are tolerable for making a Type I or Type II decision error.

The project planning team also specifies a range of possible values where the consequences of decision errors are relatively minor (the gray region). Specifying a gray region is necessary because variability in the 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. (For additional information on the gray region, hypothesis testing, and decision errors, see EPA (2000), NRC (1998), and Chapter 19, *Measurement Statistics*.)

The tolerable decision error rates are used to establish performance goals for the data collection design. Overall variability in the result can be attributed to several sources, including sample location, collection, and handling; laboratory handling and analysis; and data handling and analysis. In many environmental cases, sampling is a much larger source of uncertainty than laboratory analyses. The goal is to develop a sampling and analysis design that reduces the chance of making a wrong decision. The greater certainty demanded by the decision makers, the more comprehensive and expensive the data collection process is likely to be. In this step, the project planning team has to come to an agreement on how to determine acceptable analytical uncertainty and how good the overall data results are required to be. The team has to reach a consensus on the trade-off between the cost of more information and the increased certainty in the resulting decision.

Often the project planning team does not feel comfortable with the concepts and terminology of hypothesis testing (Type I and Type II errors, gray zone, critical region, tolerable decision error rates). As a result the project planning team may have difficulty (or want to skip) this step of the directed planning process. If these steps are skipped or insufficiently addressed, it is more likely that the data will not be of the quality needed for the project. Attachment B1 is provided to give some additional guidance on these concepts. MARLAP recommends that for each radionuclide of concern an action level, gray region and limits on decision error rates be established during a directed planning process.

Figure B2 summarizes the outputs of the decisions made by the project planning team in a Decision Performance Goal Diagram (EPA, 2000). The horizontal axis represents the (unknown) true value of the parameter being estimated. The vertical axis represents the decision maker's desired probability of concluding that the parameter exceeds an action limit. The "gray region" (bounded on one side by the action level) defines an area where the consequences of decision error are relatively minor (in other words, it defines how big a divergence from the action level we wish to distinguish). The gray region is related to the desired precision of the measurements. The height of the indicated straight lines to the right and left of the gray region depict the decision maker's tolerance for Type I and Type II errors.

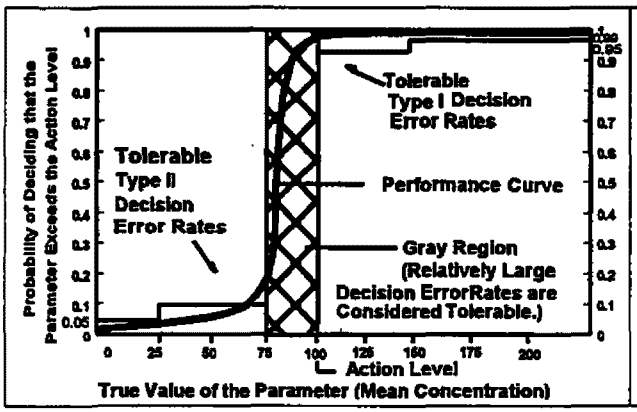

Figure B2(a)—Decision performance goal diagram null hypothesis: the parameter exceeds the action level.

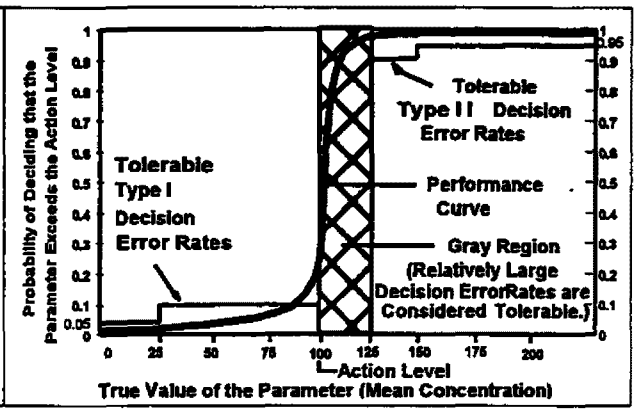

Figure B2(b)—Decision performance goal diagram null hypothesis: the parameter is less than the action level.

For purposes of this example, the default assumption (null hypothesis) was established as the measured concentration exceeded the action level (Figure B2a). The Type I error (5 percent at true concentration between 100 and 150; 1percent at >150 units) making a decision NOT to take action to solve an environmental problem (e.g., remediate) when that action was in fact required (e.g., analyte concentrations are really above an action level). The Type II error (5 percent at true concentrations <25 units; 10 percent between 25 and 75 units) is understood as taking an action when in fact that action is not required (e.g., analyte concentrations are really below the action level).

In Figure B2(b), the default assumption (null hypothesis) was established as the measured concentration is less than the action level. The Type I error (5 percent at true concentrations <25 units; 10 percent between 25 and 100 units) is understood as taking an action when in fact that action is NOT required (e.g., analyte concentrations are really below the action level). The Type II error (10 percent at true concentration between 100 and 150; 5 percent at >150 units) is understood as making a decision not to take action to solve an environmental problem (e.g., remediate) when that action was in fact required (e.g., analyte concentrations are really above an action level).

The output of Step 6 is:

- The project planning team's quantitative measure of tolerable decision error rates based on consideration of project resources.

B3.8 DQO Process Step 7: Optimize the Design for Obtaining Data

By the start of Step 7, the project planning team has established their priority of concerns, the definition of the problem, the decision or outcome to address the posed problem, the inputs and boundaries, and the tolerable decision error rates. They have also agreed on decision rules that incorporate all this information into a logic statement about what action to take in response to the decision. During Step 7, the hard decisions are made between the planning team's desire to have measurements with greater certainty and the reality of the associated resource needs (time, cost, etc.) for obtaining that certainty.

During Step 7, the project planning team optimize the sampling and analytical design and established the measurement quality objectives (MQOs) so the resulting data will meet all the established constraints in the most resource-effective manner. The goal is to determine the most efficient design (combination of sample type, sample number and analytical procedures) to meet all the constraints established in the previous steps. Once the technical specialists and the rest of the project planning team come to agreement about the sampling and analysis design, the operational details and theoretical assumptions of the selected design should be documented.

If a proposed design cannot be developed to meet the limits on decision error rates within budget or other constraints, then the project planning team will have to consider relaxing the error tolerance, adjusting the width of the gray region, redefining the scale of decision, or committing more funding. There is always a trade off between quality, cost and time. The project planning team will need to develop a consensus on how to balance resources and data quality. If the proposed design requires analysis using analytical protocols not readily available, the project planning team must consider the resources (time and cost) required to develop and validate a method, generate method detection limits relevant to media of concern, and develop appropriate QA/QC procedures and criteria (Chapter 6, *Selection and Application of an Analytical Method*).

If the project entails a preliminary investigation of a site or material for which little is known, the planners may choose to employ MQOs and requirements that typically are achieved by the selected sampling and analytical procedures. At this early point in the project, the lack of detailed knowledge of the site or material may postpone the need for the extra cost of more expensive sampling and analytical procedures and large numbers of samples, until more site or material knowledge is acquired. The less-demanding MQOs, however, should be adequate to further define the site or material. For situations when the measured values are distant from an action level the MQO-compliant data could also be sufficient to support the project decision.

The planning of data collection activities is typically undertaken to determine if a characteristic of an area or item does or does not exist above an action level. Since the area of interest (population) is usually too large to be submitted to analyses, in its entirety, these data collection activities generally include sampling. If sampling is done correctly, the field sample or set of field samples will represent the characteristics of interest and, if analyzed properly, the information gleaned from the samples can be used to make decisions about the larger area. However, if errors occur during implementation of the project, the samples and associated data may not accurately reflect the material from which the samples were collected and incorrect decisions could be made.

The planning team attempts to anticipate, quantify, and minimize the uncertainty in decisions resulting from imprecision, bias, and blunders—or in other words, attempts to manage uncertainty by managing its sources. The effort expended in managing uncertainty is project dependent and depends upon what constitutes an acceptable level of decision uncertainty and the proximity of the data to a decision point. For example, Figure B3(a) presents a situation where the data have significant variability. Yet the variability of the data does not materially add to the uncertainty of the decision since the measurements are so far removed from the action level. More resources could be expended to control the variability. However, the additional expenditure would be unnecessary, since they would not alter the decision or measurably increase confidence in the decision.

In contrast, Figure B3(b) depicts data with relatively little variability, yet this level of variability is significant since the measured data are adjacent to the action level, which results in increased uncertainty in the decision. Depending upon the consequences of an incorrect decision, it may be advisable to expend more resources with the intention of increasing confidence in the decision.

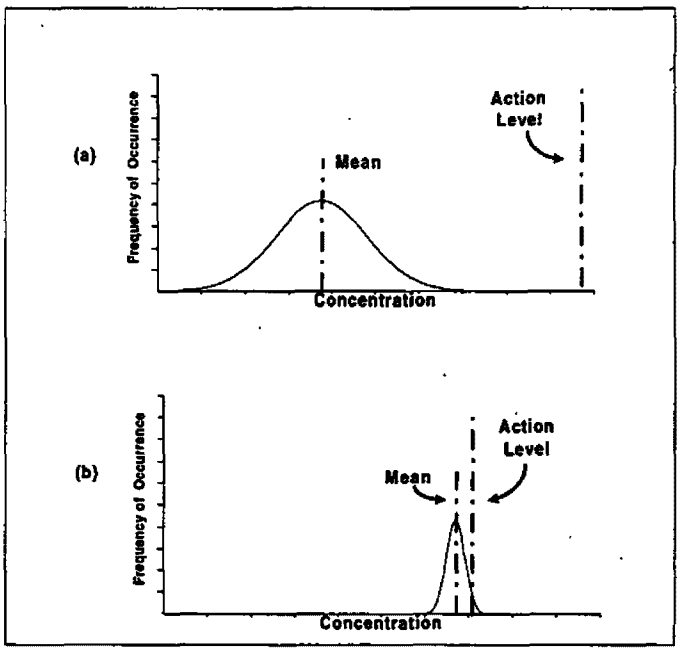

Figure B3 — How Proximity to the action level determines what is an acceptable level of uncertainty.

The output of Step 7 is:

- The most resource-effective design for sampling and analysis that will obtain the specific amount and quality of data needed to resolve the problem within the defined constraints; and

- Detailed plans and criteria for data assessment.

B3.9 References

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ATTACHMENT B-1 DECISION ERROR RATES AND THE GRAY REGION

B-1.1 Introduction

This attachment is provided to present some additional discussion on decision error rates and the gray region. The project planning team will need to specify a range of possible values where the consequences of decision errors are relatively minor—the "gray region." Specifying a gray region is necessary because variability in the 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.

B-1.2 The Region of Interest

The first step in constructing the gray region is setting the range of concentrations that is a region of interest (a range of possible values). Usually there is an action level (such as the derived concentration guideline level, a regulatory limit) that should not be exceeded. If the project planning team wants a method to measure sample concentrations around this level, they would not select one that worked at concentrations at 10 to 100 times the action level, nor would they select one that worked from zero to half the action level. They would want a method that worked well around the action level—perhaps from 0.1 to 10 times the action level, or from one-half to two times the action level. For the purpose of the example in this attachment, the action level is 1.0 and the project planning team selected a region of interest that is zero to twice the action level (0-2), as shown on the x-axis in Figure B-1.1.

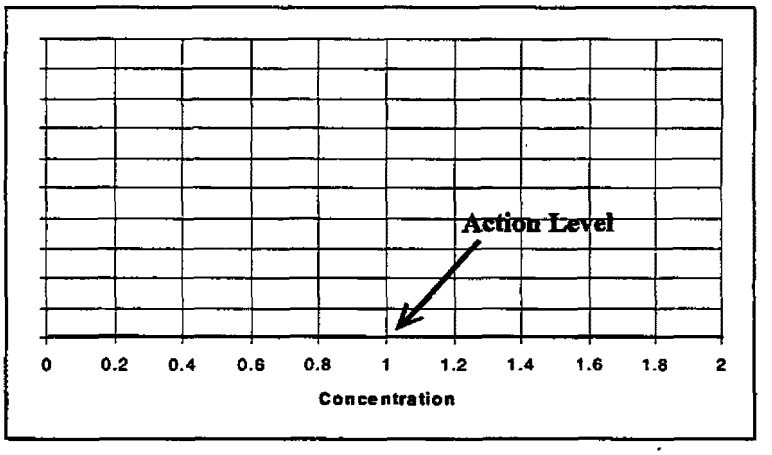

FIGURE B-1.1

B-1.3 Measurement Uncertainty at the Action Level

The action level marks the concentration level that the project planning team must be able to distinguish. The project planning team wants to be able to tell if the measured concentration is above or below the action level. Does this mean that the project planning team needs to be able to distinguish 0.9999 times the action level from 1.0001 times the action level? Sometimes, but not usually. This is fortunate, because current measurement techniques are probably not good enough to distinguish that small a difference in concentrations.

How close to the action level can the project planning team plan to measure? For this example, we will assume that the standard uncertainty (1 sigma, σ) of the measured concentration is 10 percent of the action level. With that kind of measurement "precision," can the project planning team tell the difference between a sample with 0.9 times the action level from one right at the action level? Not always. Figure B-1.2 shows the distribution of the concentration that is measured (assuming a normal distribution). This means that about 16 percent of the time, the measured concentration (in the shaded area) will appear to be 0.9 times the action level or less, even though the true concentration is exactly equal to the action level.

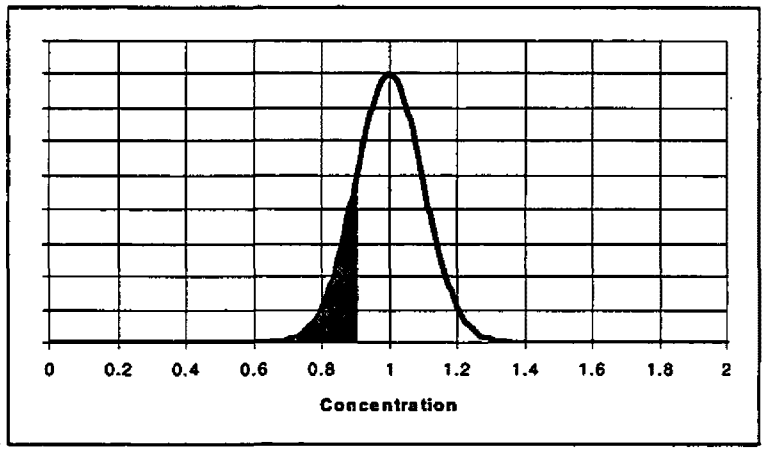

FIGURE B-1.2

Similarly, about 16 percent of the time, the measured concentration will appear to be at or above the action level (as shown in the shaded area in Figure B-1.3), even though the true concentration is only 0.9 times the action level.

The problem is, when there is only the measurement result to go by, the project planning team cannot tell the

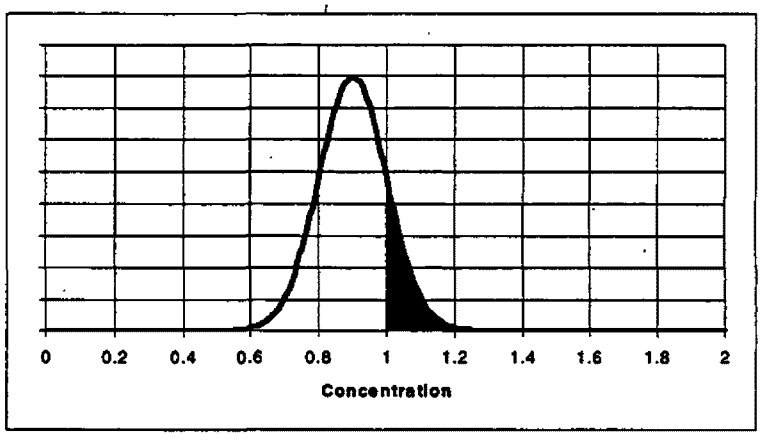

FIGURE B-1.3

difference with confidence. If the measured concentration is 0.9, it is more likely that the true concentration is 0.9 than it is 1.0, but there remains a chance that it is really 1.0.

B-1.4 The Null Hypothesis

If the measured concentration is 0.95, it is equally likely that the true concentration is 0.9 as it is 1.0 (see Figure B-1.4). How does the project planning team decide what is the true concentration? The project planning team starts by asking:

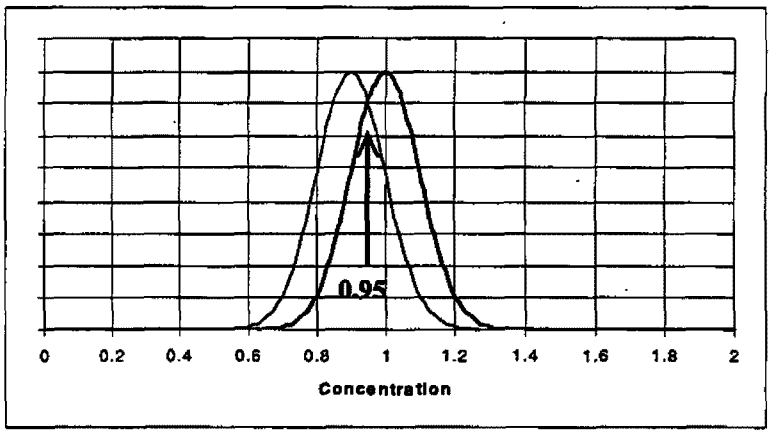

FIGURE B-1.4

"Which mistake is worse: (1) saying the true concentration is 0.9 when it is 1.0 or more? or (2) saying the true concentration is 1.0 when it is 0.9 or less?"

What does the project planning team mean by "worse"? The project planning team really does not want to make a mistake that is likely to remain undiscovered or will be difficult or expensive to correct.

Case 1: Assume The True Concentration is Over 1.0

If a true concentration of 1.0 or more is over a regulatory limit, the project planning team will not want to make mistake (1) above. If the project planning team decides the true concentration is less than 1.0, the project planning team is not likely to look at the sample again. That would mean that the mistake would probably not be discovered until much later, if at all. On the other hand, if the project planning team decides that the true concentration is over 1.0 when it really is not, the project planning team will discover the mistake while they are trying to figure out how to "correct" the high reading. So the project planning team will make a rule: Assume the true concentration is over 1.0 unless they are really sure it is under. This is the default assumption, the "null hypothesis."

How sure does the project planning team need to be? For this example, we will assume that the project planning team would like to be 95 percent sure. To be 95 percent sure, they would have to

stay with their assumption that the true concentration is over 1.0 unless the measured concentration is 0.84 or less (Figure B-1.5). The project planning team knows that this will only happen about 5 percent of the time when the true concentration is really 1.0. That is, the measurement has to be less than 0.84 to be 95 percent sure the true concentration is less than 1.0.

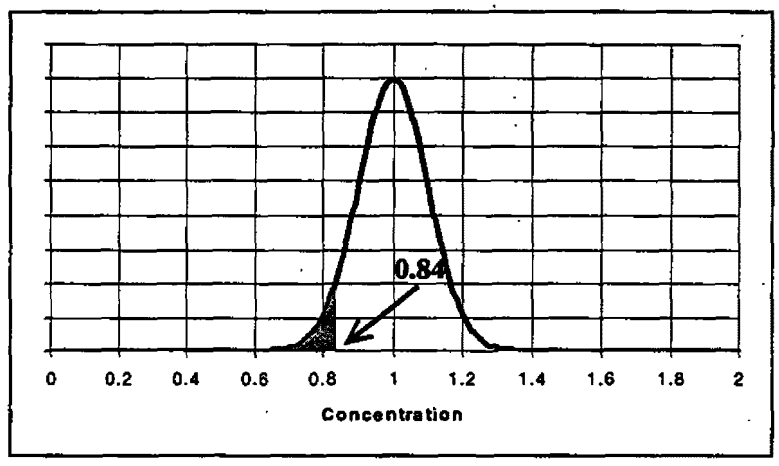

FIGURE B-1.5

But what if the true concentration is 0.9 or less—mistake (2) above? Under the new rule (default assumption or null hypothesis), how often will the project planning team say that the true concentration is over 1.0 when it is really only 0.84? As seen in Figure B-1.6, there is only a 50-50 chance of making the right decision when the true concentration really is 0.84. That is the price of being sure they are not over the action level.

How low does the true concentration have to be in order to have a pretty good chance of deciding that the true concentration is below the limit? To be 95 percent sure, the true concentration needs to be twice as far below the action level as the decision point, namely at about 0.68. That is, the project planning team will need a concentration of 0.68 or less to be 95 percent sure that they will be able to decide the true concentration is less than 1.0 (see the unshaded portion in Figure B-1.7). In other words, it is only when the true concentration is 0.68 or less that the project planning team can be pretty sure that they will decide the true concentration is less than 1.0. (Note how similar this looks to an MDC in reverse.)

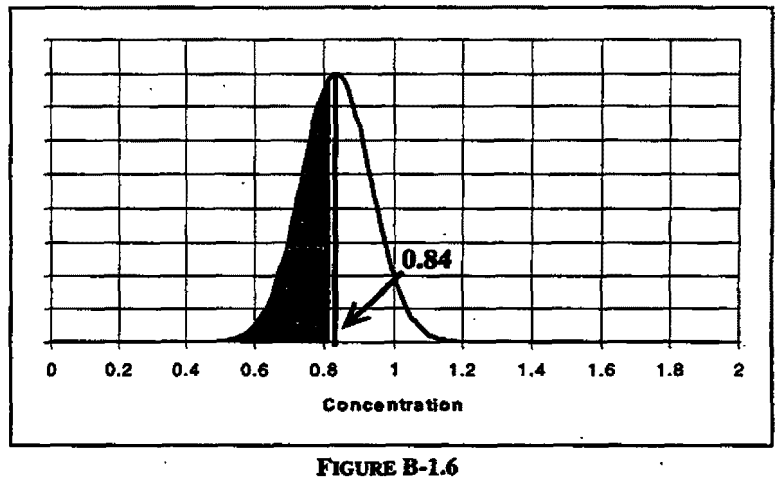

FIGURE B-1.6

Case 2: Assume The True Concentration is 0.9

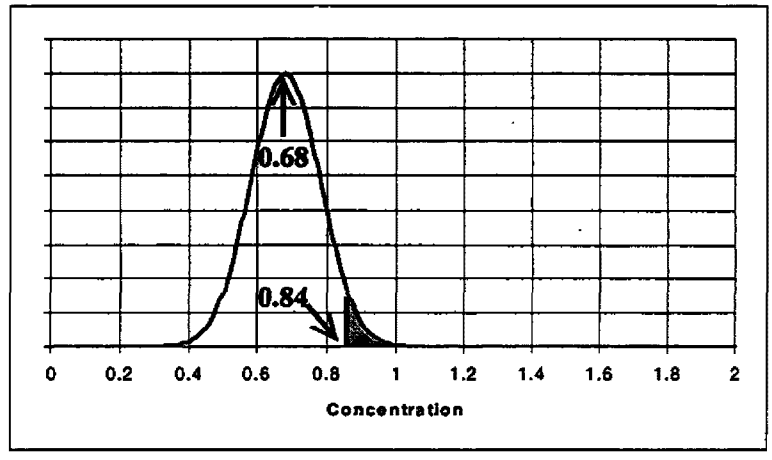

FIGURE B-1.7

As stated previously, the mistake that is most serious determines the null hypothesis. Suppose that the project planning team determined that it is worse to decide that the true concentration is over 1.0 when it is 0.9 (than it is to decide it is 0.9 when it is 1.0). Then, the default assumption (the null hypothesis) would be that the true concentration is 0.9, unless the measured concentration is large enough to convince the planning team otherwise. Only when the measured concentration reaches 1.06 does the planning team decide the true concentration is over 1.0 (Figure B-1.8). The team will have to have a true concentration of 1.22 or more to be 95 percent sure that they will be able to decide the true concentration is over 1.0.

B-1.5 The Critical Region

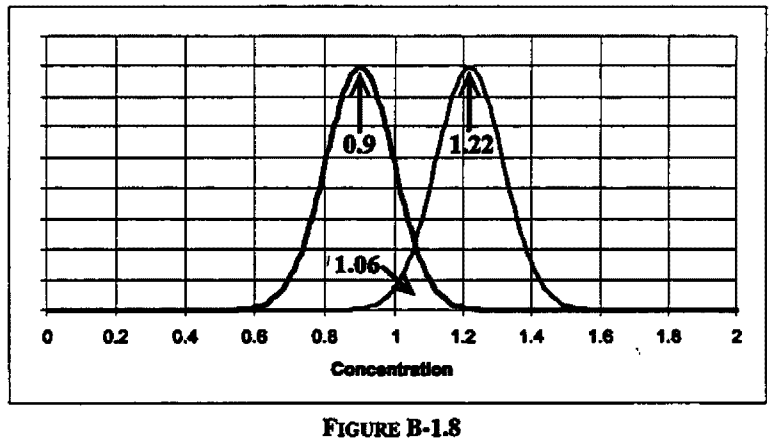

FIGURE B-1.8

The mistake that is "worse" defines the null hypothesis and also defines a "Type I" error. The probability of a Type I error happening is called the "Type I error rate," and is denoted by alpha (α). Under the original null hypothesis (Case 1: Assume the true concentration is over 1.0), a Type I error would be deciding that the concentration was less than 1.0 when it really was not. In general, a Type I error is deciding against the null hypothesis when it is actually true. (A Type I error is also called a "false positive." This can be confusing when the null hypothesis appears to be a "positive" statement. Therefore, MARLAP uses the neutral terminology.)

The "less serious" mistake is called a Type II error, and the probability of it happening is the "Type II error rate," denoted by beta (β). Under the original null hypothesis that the concentration

was 1.0 or more, a Type II error would be deciding that the concentration was more than 1.0 when it really was not. In general, a Type II error is not deciding against the null hypothesis when it is actually false.

In both Case 1 and Case 2, the probability of both Type I errors and Type II errors were set to 5 percent. The probabilities were calculated at multiples of the standard deviation, assuming a normal distribution. This will not always be the case. However, the probability of a Type I error is always calculated as the probability that the project planning team will decide to reject the null hypothesis when it is actually true. This is simple enough, as long as there is a clear boundary for the parameter of interest.

The parameter of interest in both Case 1 and Case 2 was the true concentration. The true concentration had a limit of 1.0. Therefore, all the project planning team had to do was calculate the probability that they would get a measured concentration that would cause them to decide that the true concentration was less than 1.0, even though it was equal to 1.0. In the example, the project planning team actually started with the probability (5 percent) and worked out the critical value. The "critical value" (or decision point) is the measured value that divides the measurement results into two different sets: (1) those values that will cause us to reject the null hypothesis and (2) those values that will cause us to leave the null hypothesis as the default. Set (1) is called the "critical region."

The Type I and Type II error rates, α and β, often are both set at 5 percent. This is only by tradition. They do not have to be equal. Neither error rate needs to be set at 5 percent. The way the project planning team should set the value is by examining the consequences of making a Type I or a Type II error. What consequences will happen as a result of making each type of error? This is a little different than the criterion that was used to define the null hypothesis. It may be that in some circumstances, a Type II error is riskier than a Type I error. In that case, consider making α bigger than β

B-1.6 The Gray Region

In the previous sections (B-1.1 to B-1.4) the project planning team:

- Set the region of interest for the measured concentrations between zero and about twice the action level;

- Assumed that the true concentration exceeds 1.0, unless they measure "significantly" below that, the default assumption (null hypothesis);

- Defined "significantly below" to mean a concentration that would be observed less than 5 percent of the time, when the true concentration is actually 1.0. To describe their uncertainty, the project planning team used the normal distribution, with a relative standard deviation of 10 percent at the action level, as a model;

- Developed an operational decision rule: If the measured concentration is less than 0.84, then decide the true concentration is less than 1.0. Otherwise, decide there is not enough reason to change the default assumption (null hypothesis); and

- Found using this operational decision rule that they were pretty sure (95 percent) of deciding that the true concentration is less than 1.0 only when the true concentration is actually 0.68 or less.

If the true concentration is between 0.68 and 1.0, all the project planning team really can say is that the probability of deciding that the true concentration is less than 1.0 will be between 5 percent (when the true concentration is 1.0) and 95 percent (when the true concentration is 0.68). Conversely, when the true concentration is in this range, the probability of deciding that the true concentration is not less than 1.0 (i.e., the probability of a Type II error) will be between 5 percent (when the true concentration is 0.68) and 95 percent (when the true concentration is just under 1.0). This range of concentrations is called the "gray region."

When the null hypothesis is that the true concentration exceeds the action level (1.0), the gray region is bounded from above by the action level. This is where α is set. It is bounded from below at the concentration where β is set. There is some flexibility in setting the lower boundary of the gray region (LBGR). If the project planning team specifies a concentration, they can calculate the probability β. If they specify β, they can calculate the value of the true concentration that will be correctly detected as being below 1.0 with probability $1-\beta$.

In our example, the project planning team found that they needed the true concentration to be 0.68 or less to be at least 95 percent sure that they will correctly decide (by observing a measured value of 0.84 or less) that the true concentration is less than 1.0. If the project planning team doesn't like that, the project planning team can find that a true concentration of 0.71 will be correctly detected 90 percent of the time (also by observing a measured value of 0.84 or less). The critical value, or decision point, is determined by α, not β.

If the project planning team decides to raise the LBGR (i.e., narrow the gray region) the Type II error rate at the LBGR goes up. If they lower the LBGR (i.e., widen the gray region) the Type II

error rate at the LBGR goes down. Nothing substantive is really happening. The project planning team is merely specifying the ability to detect that the null hypothesis is false.

If the project planning team wants to make a substantive change, they need to change the probability that an error is made. That is, they need to change the uncertainty (standard deviation) of the measurements. Suppose the relative standard deviation of the measurements at the action level is 5 percent instead of 10 percent. Then the value of the true concentration that will be correctly detected to be below the action level (by observing a measured value of 0.92 or less) 95 percent of the time, is 0.84. Cutting the standard deviation of the measurement in half has cut the (absolute) width of the gray region in half, but left the width of the gray region in standard deviations unchanged. Previously, with $\sigma = 10$ percent, the width of the gray region was $1.0 - 0.68 = 0.32 = 3.2\ (0.10) = 3.2\sigma$. As Figure B-1.9 illustrates, with $\sigma = 5$ percent, the width of the gray region is $1.0 - 0.84 = 0.16 = 3.2\ (0.05) = 3.2\sigma$.

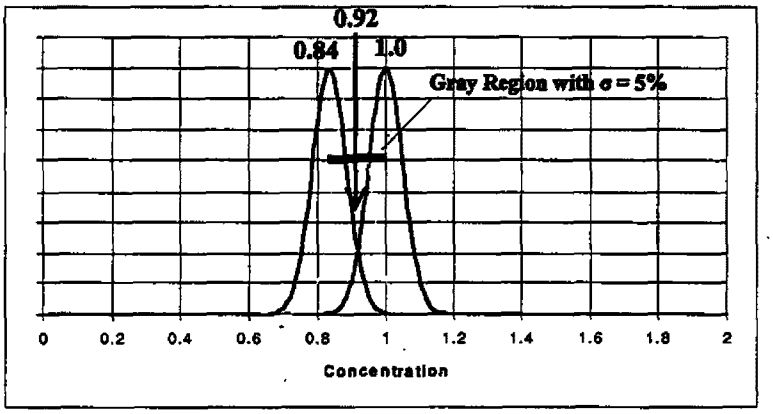

FIGURE B-1.9

What is important is the width of the gray region in standard deviations; not the width of the gray region in concentration. In order to achieve the same specified Type II error rate at the LBGR, the action level and the LBGR must be separated by the same number of standard deviations. The width of the gray region (action level minus LBGR) will be denoted by delta (Δ), the "shift." Δ/σ is how many standard deviations wide the gray region is. Δ/σ is called the "relative shift."

If the gray region is less than one standard deviation wide, the Type II error rate may be high at the LBGR. The only way to improve the situation would be to decrease the standard deviation (i.e., increase the relative shift, Δ/σ). This can be done by employing a more precise measurement method or by averaging several measurements. When the width of the gray region is larger than about three standard deviations (i.e., Δ/σ exceeds 3), it is overkill. It may be possible to use a simpler, less expensive measurement method or take fewer samples.

APPENDIX C
MEASUREMENT QUALITY OBJECTIVES FOR METHOD UNCERTAINTY AND DETECTION AND QUANTIFICATION CAPABILITY

C.1 Introduction

This appendix expands on issues related to measurement quality objectives (MQOs) for several method performance characteristics which are introduced in Chapter 3, *Key Analytical Planning Issues and Developing Analytical Protocol Specifications*. Specifically, this appendix provides the rationale and guidance for establishing project-specific MQOs for the following method performance characteristics: method uncertainty, detection capability and quantification capability. In addition, it provides guidance in the development of these MQOs for use in the method selection process and guidance in the evaluation of laboratory data based on the MQOs. Section C.2 is a brief overview of statistical hypothesis testing as it is commonly used in a directed planning process, such as the Data Quality Objectives (DQO) Process (EPA 2000). More information on this subject is provided in Chapter 2, *Directed Planning Process* and Appendix B, *The Data Quality Objectives Process*. Section C.3 derives MARLAP's recommended criteria for establishing project-specific MQOs for method uncertainty, detection capability, and quantification capability. These criteria for method selection will meet the requirements of a statistically based decision-making process. Section C.4 derives MARLAP's recommended criteria for evaluation of the results of quality control analyses by project managers and data reviewers (see also Chapter 8, *Radiochemical Data Verification and Validation*).

It is assumed that the reader is familiar with the concepts of measurement uncertainty, detection capability, and quantification capability, and with terms such as "standard uncertainty," "minimum detectable concentration," and "minimum quantifiable concentration," which are introduced in Chapter 1, *Introduction to MARLAP*, and discussed in more detail in Chapter 19, *Measurement Statistics*. MARLAP also uses the term "method uncertainty" to refer to the predicted uncertainty of the result that would be measured if the method were applied to a hypothetical laboratory sample with a specified analyte concentration. The method uncertainty is a characteristic of the analytical method and the measurement process.

C.2 Hypothesis Testing

Within the framework of a directed planning process, one considers an *action level*, denoted here by AL, which is the contaminant concentration in either a population (e.g., a survey unit) or an individual item (e.g., a laboratory sample) that should not be exceeded. Statistical hypothesis testing is used to decide whether the actual contaminant concentration X is greater than AL. For more information on this topic, see EPA QA/G-4, MARSSIM, NUREG-1505 (EPA 2000, MARSSIM 2000, NRC 1998), or Appendix B of this manual.

In hypothesis testing, one formulates two hypotheses about the value of X, and evaluates the measurement data to choose which hypothesis to accept and which to reject.[1] The two hypotheses are called the *null hypothesis* H_0 and the *alternative hypothesis* H_1. They are mutually exclusive and together describe all possible values of X under consideration. So, in any given situation, one and only one of the hypotheses must be true. The null hypothesis is presumed true unless the data provide evidence to the contrary. Thus the choice of the null hypothesis determines the burden of proof in the test.

Most often, if the action level is not zero, one assumes it has been exceeded unless the measurement results provide evidence to the contrary. In this case, the null hypothesis is H_0: $X \geq$ AL and the alternative hypothesis is H_1: $X <$ AL. If one instead chooses to assume the action level has not been exceeded unless there is evidence to the contrary, then the null hypothesis is H_0: $X \leq$ AL and the alternative hypothesis is H_1: $X >$ AL. The latter approach is the only reasonable one if AL = 0, because it is virtually impossible to obtain statistical evidence that an analyte concentration is exactly zero.

In any hypothesis test, there are two possible types of decision errors. A *Type I* error occurs if the null hypothesis is rejected when it is, in fact, true. A *Type II* error occurs if the null hypothesis is not rejected when it is false.[2] Since there is always measurement uncertainty, one cannot eliminate the possibility of decision errors. So instead, one specifies the maximum Type I decision error rate α that is allowable when the contaminant concentration is at or above the action

[1] In hypothesis testing, to "accept" the null hypothesis only means not to reject it, and for this reason many statisticians avoid the word "accept" in this context. A decision not to reject the null hypothesis does not imply the null hypothesis has been shown to be true.

[2] The terms "false positive" and "false negative" are synonyms for "Type I error" and "Type II error," respectively. However, MARLAP deliberately avoids these terms here, because they may be confusing when the null hypothesis is an apparently "positive" statement, such as $X \geq$ AL.

level AL. This maximum usually occurs when the concentration is exactly equal to AL. The most commonly used value of α is 0.05, or 5%. One also chooses another concentration DL (the "discrimination limit") that one wishes to be able to distinguish reliably from the action level. One specifies the maximum Type II decision error rate β that is allowable when the contaminant concentration equals DL, or, equivalently, the "power" $1 - \beta$ of the statistical test at $X = \text{DL}$. The *gray region* is then defined as the interval between the two concentrations AL and DL.

The gray region is a set of concentrations close to the action level, where one is willing to tolerate a Type II decision error rate that is higher than β. For concentrations above the upper bound of the gray region or below the lower bound, the decision error rate is no greater than the specified value (either α or β as appropriate). Ideally, the gray region should be narrow, but in practice, its width is determined by balancing the costs involved, including the cost of measurements and the estimated cost of a Type II error, possibly using prior information about the project and the parameter being measured.

If H_0 is $X \geq$ AL (presumed contaminated), then the upper bound of the gray region is AL and the lower bound is DL. If H_0 is $x \leq$ AL (presumed uncontaminated), then the lower bound of the gray region is AL and the upper bound is DL. Since no assumption is made here about which form of the null hypothesis is being used, the lower and upper bounds of the gray region will be denoted by LBGR and UBGR, respectively, and not by AL and DL. The width of the gray region (UBGR – LBGR) is denoted by Δ and called the *shift* or the required *minimum detectable difference* in concentration (EPA 2000, MARSSIM 2000, NRC 1998). See Appendix B, *The Data Quality Objectives Process*, for graphical illustrations of these concepts.

Chapter 3 of MARLAP recommends that for each radionuclide of concern, an action level, gray region, and limits on decision error rates be established during a directed planning process. Section C.3 presents guidance on the development of MQOs for the selection and development of analytical protocols. Two possible scenarios are considered. In the first scenario, the parameter of interest is the mean analyte concentration for a sampled population. The question to be answered is whether the population mean is above or below the action level. In the second scenario a decision is to be made about individual items or specimens, and not about population parameters. This is the typical scenario in bioassay, for example. Some projects may involve both scenarios. For example, project planners may want to know whether the mean analyte concentration in a survey unit is above an action level, but they may also be concerned about individual samples with high analyte concentrations.

C.3 Development of MQOs for Analytical Protocol Selection

This section derives MARLAP's recommendations for establishing MQOs for the analytical protocol selection and development process. Guidance is provided for establishing project-specific MQOs for method uncertainty, detection capability, and quantification capability. Once selected, these MQOs are used in the initial, ongoing, and final evaluations of the protocols. MARLAP considers two scenarios and develops MQOs for each.

SCENARIO I: A Decision Is to Be Made about the Mean of a Sampled Population

In this scenario the total variance of the data σ^2 is the sum of two components

$$\sigma^2 = \sigma_M^2 + \sigma_S^2$$

where σ_M^2 is the average analytical method variance (M = "method") and σ_S^2 is the variance of the sampled population. The sampling standard deviation σ_S may be affected by the spatial and temporal distribution of the analyte, the extent of the survey unit, the physical sample sizes, and the sample collection procedures. The analytical standard deviation σ_M is affected by laboratory sample preparation, subsampling, and analysis procedures. The value of σ_M may be estimated by the *combined standard uncertainty* of a measured value for a sample whose concentration equals the hypothesized population mean concentration (see Chapter 19, *Measurement Statistics*).

The ratio Δ / σ, called the "relative shift," determines the number of samples required to achieve the desired decision error rates α and β. The target value for this ratio should be between 1 and 3, as explained in MARSSIM and NUREG-1505 (MARSSIM 2000, NRC 1998). Ideally, to keep the required number of samples low, one prefers that $\Delta / \sigma \approx 3$. The cost in number of samples rises rapidly as the ratio Δ / σ falls below 1, but there is little benefit from increasing the ratio much above 3.

Generally, it is easier to control σ_M than σ_S. If σ_S is known (approximately), a target value for σ_M can be determined. For example, if $\sigma_S < \Delta / 3$, then a value of σ_M no greater than $\sqrt{\Delta^2/9 - \sigma_S^2}$ ensures that $\sigma \le \Delta / 3$, as desired. If $\sigma_S > \Delta / 3$, the requirement that the total σ be less than $\Delta / 3$ cannot be met regardless of σ_M. In the latter case, it is sufficient to make σ_M negligible in comparison to σ_S.

Often one needs a method for choosing σ_M in the absence of specific information about σ_S. In this situation, MARLAP recommends the requirement $\sigma_M \le \Delta / 10$ by default. The recommendation is justified below.

Since it is desirable to have $\sigma \le \Delta / 3$, this condition is adopted as a primary requirement. Assume for the moment that σ_S is large. Then σ_M should be made negligible by comparison. Generally, σ_M is considered negligible if it is no greater than about $\sigma_S / 3$. When this condition is met, further reduction of σ_M has little effect on σ and therefore is usually not cost-effective. So, the inequality $\sigma_M \le \sigma_S / 3$ is adopted as a second requirement.

Algebraic manipulation of the equation $\sigma^2 = \sigma_M^2 + \sigma_S^2$ and the required inequality $\sigma_M \le \sigma_S / 3$ gives

$$\sigma_M \le \frac{\sigma}{\sqrt{10}}$$

The inequalities $\sigma \le \Delta / 3$ and $\sigma_M \le \sigma / \sqrt{10}$ together imply the requirement

$$\sigma_M \le \frac{\Delta}{3\sqrt{10}}$$

or approximately

$$\sigma_M \le \frac{\Delta}{10}$$

The required upper bound for the standard deviation σ_M will be denoted by σ_{MR}. MARLAP recommends

$$\sigma_{MR} = \frac{\Delta}{10}$$

by default as a requirement in Scenario I when σ_S is unknown. This upper bound was derived from the assumption that σ_S was large, but it also ensures that the primary requirement $\sigma \le \Delta / 3$ will be met if σ_S is small. When the analytical standard deviation σ_M is less than σ_{MR}, the primary requirement will be met unless the sampling variance σ_S^2 is so large that σ_M^2 is negligible by comparison, in which case little benefit can be obtained from further reduction of σ_M.

The recommended value of σ_{MR} is based on the assumption that any known bias in the measurement process has been corrected and that any remaining bias is much smaller than the shift, Δ, when a concentration near the gray region is measured.

Achieving an analytical standard deviation σ_M less than the recommended limit, $\Delta / 10$, may be difficult in some situations, particularly when the shift, Δ, is only a fraction of UBGR. When the recommended requirement for σ_M is too costly to meet, project planners may allow σ_{MR} to be

larger, especially if σ_S is believed to be small or if it is not costly to analyze the additional samples required because of the larger overall data variance ($\sigma_M^2 + \sigma_S^2$). In this case, project planners may choose σ_{MR} to be as large as $\Delta / 3$ or any calculated value that allows the data quality objectives to be met at an acceptable cost.

The true standard deviation, σ_M, is a theoretical quantity and is never known exactly, but the laboratory may estimate its value using the methods described in Chapter 19, and Section 19.6.13 in particular. The laboratory's estimate of σ_M will be denoted here by u_M and called the "method uncertainty." The method uncertainty, when estimated by uncertainty propagation, is the predicted value of the combined standard uncertainty ("one-sigma" uncertainty) of the analytical result for a laboratory sample whose concentration equals UBGR. Note that the term "method uncertainty" and the symbol u_M actually apply not only to the method but to the entire measurement process.

In theory, the value σ_{MR} is intended to be an upper bound for the true standard deviation of the measurement process, σ_M, which is unknown. In practice, σ_{MR} is actually used as an upper bound for the method uncertainty, u_M, which may be calculated. Therefore, the value of σ_{MR} will be called the "required method uncertainty" and denoted by u_{MR}. As noted in Chapter 3, MARLAP recommends that project planners specify an MQO for the method uncertainty, expressed in terms of u_{MR}, for each analyte and matrix.

The MQO for method uncertainty is expressed above in terms of the required standard deviation of the measurement process for a laboratory sample whose analyte concentration is at or above the upper bound of the gray region, UBGR. In principle the same MQO may be expressed as a requirement that the minimum quantifiable concentration (MQC) be less than or equal to UBGR. Chapter 19 defines the MQC as the analyte concentration at which the relative standard deviation of the measured value (i.e., the relative method uncertainty) is $1 / k_Q$, where k_Q is some specified positive value. The value of k_Q in this case should be specified as $k_Q = \text{UBGR} / u_{MR}$. In fact, if the lower bound of the gray region is zero, then one obtains $k_Q = 10$, which is the value most commonly used to define the MQC in other contexts. In practice the requirement for method uncertainty should only be expressed in terms of the MQC when $k_Q = 10$, since to define the MQC with any other value of k_Q may lead to confusion.

EXAMPLE: Suppose the action level is 1 Bq/kg and the lower bound of the gray region is 0.6 Bq/kg. If decisions are to be made about survey units based on samples, then the required method uncertainty at 1 Bq/kg is

$$u_{MR} = \frac{\Delta}{10} = \frac{1 - 0.6}{10} = 0.04 \text{ Bq/kg}$$

If this uncertainty cannot be achieved, then an uncertainty as large as $\Delta / 3 = 0.13$ Bq/kg may be allowed if σ_S is small or if more samples are taken per survey unit.

A common practice in the past has been to select an analytical method based on the *minimum detectable concentration* (MDC), which is defined in Chapter 19, *Measurement Statistics*. For example, the Multi-Agency Radiation Survey and Site Investigation Manual (MARSSIM 2000) says:

> During survey design, it is generally considered good practice to select a measurement system with an MDC between 10-50% of the DCGL [action level].

Such guidance implicitly recognizes that for cases when the decision to be made concerns the mean of a population that is represented by multiple laboratory samples, criteria based on the MDC may not be sufficient and a somewhat more stringent requirement is needed. It is interesting to note that the requirement that the MDC (about 3 times σ_M) be 10–50% of the action level is tantamount to requiring that σ_M be 0.03 to 0.17 times the action level — i.e. the relative standard deviation should be approximately 10% at the action level. Thus, the requirement is more naturally expressed in terms of the MQC.

SCENARIO II: Decisions Are to Be Made about Individual Items

In this scenario, the total variance of the data equals the analytical variance, σ_M^2. Consequently the data distribution in most instances should be approximately normal. The decision in this case may be made by comparing the measured concentration, x, plus or minus a multiple of its combined standard uncertainty to the action level, AL. The combined standard uncertainty, $u_c(x)$, is assumed to be an estimate of the true standard deviation of the measurement process as applied to the item being measured; so, the multiplier of $u_c(x)$ equals $z_{1-\alpha}$, the $(1-\alpha)$-quantile of the standard normal distribution (see Appendix G, *Statistical Tables*).

Alternatively, if AL is zero, so that any detectable amount of analyte is of concern, the decision may involve comparing x to the critical value of the concentration, x_C, as defined in Chapter 19, *Measurement Statistics*.

Case II-1: Suppose the null hypothesis is $x \geq$ AL, so that the action level, AL, equals the upper bound of the gray region, UBGR. Given the analytical variance σ_M^2, only a measured result that is less than about UBGR $- z_{1-\alpha}\sigma_M$ will be judged to be clearly less than the action level. Then the desired power of the test $1 - \beta$ is achieved at the lower bound of the gray region only if LBGR $\leq$ UBGR $- z_{1-\alpha}\sigma_M - z_{1-\beta}\sigma_M$. Algebraic manipulation transforms this requirement to

$$\sigma_M \leq \frac{\text{UBGR} - \text{LBGR}}{z_{1-\alpha} + z_{1-\beta}} = \frac{\Delta}{z_{1-\alpha} + z_{1-\beta}}$$

Case II-2: Suppose the null hypothesis is $x \leq$ AL, so that the action level, AL, equals the lower bound of the gray region, LBGR. Then only a measured result that is greater than about LBGR + $z_{1-\alpha}\sigma_M$ will be judged to be clearly greater than the action level. Then the desired power of the test $1 - \beta$ is achieved at the upper bound of the gray region only if UBGR $\geq$ LBGR + $z_{1-\alpha}\sigma_M$ + $z_{1-\beta}\sigma_M$. Algebraic manipulation transforms this requirement to

$$\sigma_M \leq \frac{\text{UBGR} - \text{LBGR}}{z_{1-\alpha} + z_{1-\beta}} = \frac{\Delta}{z_{1-\alpha} + z_{1-\beta}}$$

So, in either case, we have the requirement:

$$\sigma_M \leq \frac{\Delta}{z_{1-\alpha} + z_{1-\beta}}$$

Therefore, MARLAP recommends the use of

$$u_{MR} = \sigma_{MR} = \frac{\Delta}{z_{1-\alpha} + z_{1-\beta}}$$

as an MQO for method uncertainty when decisions are to be made about individual items (i.e., laboratory samples) and not about population parameters.

If both α and β are at least 0.05, one may use the value $u_{MR} = 0.3\Delta$.

If LBGR = 0, then Δ = UBGR and $\sigma_{MR} = \Delta / (z_{1-\alpha} + z_{1-\beta})$ implies

$$\sigma_M \leq \frac{\text{UBGR}}{z_{1-\alpha} + z_{1-\beta}}$$

This requirement is essentially equivalent to requiring that the MDC not exceed UBGR. Thus, when LBGR = 0, the MQO may be expressed in terms of the detection capability of the analytical method.

Note that when AL = LBGR = 0, the MQO for detection capability may be derived directly in terms of the MDC, since the MDC is defined as the analyte concentration at which the probability of detection is $1 - \beta$ when the detection criterion is such that the probability of false detection in a sample with zero analyte concentration is at most α.

EXAMPLE: Suppose the action level is 1 Bq/L, the lower bound of the gray region is 0.5 Bq/L, $\alpha = 0.05$, and $\beta = 0.10$. If decisions are to be made about individual items, then the required method uncertainty at 1 Bq/L is

$$u_{MR} = \frac{\Delta}{z_{1-\alpha} + z_{1-\beta}} = \frac{1 - 0.5}{z_{0.95} + z_{0.90}} = \frac{0.5}{1.645 + 1.282} = 0.17 \text{ Bq/L.}$$

C.4 The Role of the MQO for Method Uncertainty in Data Evaluation

This section provides guidance and equations for determining warning and control limits for QC sample results based on the project-specific MQO for method uncertainty. In the MARLAP Process as described in Chapter 1, these warning and control limits are used in the ongoing evaluation of protocol performance (see Chapter 7, *Evaluating Protocols and Laboratories*) and in the evaluation of the laboratory data (see Chapter 8, *Radiochemical Data Verification and Validation).*

C.4.1 Uncertainty Requirements at Various Concentrations

When project planners follow MARLAP's recommendations for establishing MQOs for method uncertainty for method selection and development, the maximum allowable standard deviation,

σ_{MR}, at the upper bound of the gray region (UBGR) is specified. During subsequent data evaluation, the standard deviation at any concentration less than UBGR should be at most σ_{MR}, and the relative standard deviation at any concentration greater than UBGR should be at most σ_{MR} / UBGR, which will be denoted here by φ_{MR}. Note that, since the true standard deviation can never be known exactly, in practice the requirement is expressed in terms of the required method uncertainty, u_{MR}, to which the combined standard uncertainty of each result may be compared.

EXAMPLE: Consider the preceding example, in which AL = UBGR = 1 Bq/L, LBGR = 0.5 Bq/L, and u_{MR} = 0.17 Bq/L. In this case the combined standard uncertainty for any measured result x should be at most 0.17 Bq/L if $x < 1$ Bq/L, and the relative combined standard uncertainty should be at most 0.17 / 1, or 17%, if $x > 1$ Bq/L.

In Scenario I, where decisions are made about the mean of a population based on multiple physical samples (e.g., from a survey unit), if the default value $\sigma_{MR} = \Delta / 10$ is assumed for the required method uncertainty, then the required bound for the analytical standard deviation as a function of concentration is as shown in Figure C.1 below. The figure shows that the bound, σ_{Req}, is constant at all concentrations, x, below UBGR, and σ_{Req} increases with x when x is above UBGR. So, $\sigma_{Req} = \sigma_{MR}$ when $x <$ UBGR and $\sigma_{Req} = x \cdot \sigma_{MR}$ / UBGR when $x >$ UBGR.

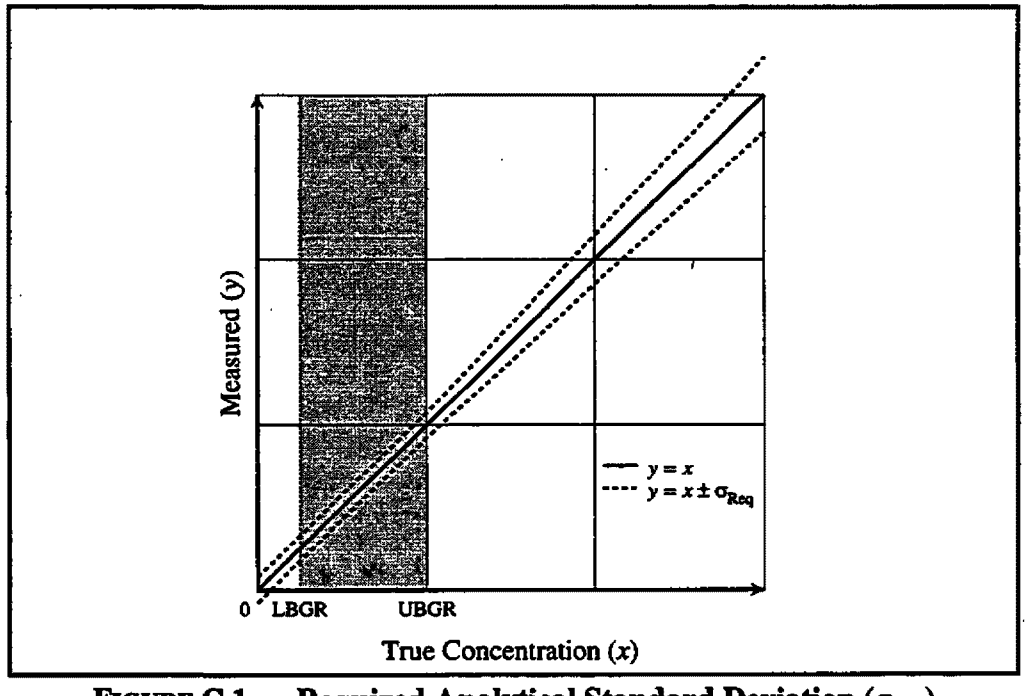

FIGURE C.1 — Required Analytical Standard Deviation (σ_{Req})

These requirements can be relaxed somewhat for samples with very high analyte concentrations as long as the project's requirements for decision uncertainty are met. However, MARLAP does not provide specific guidance to address this issue for Scenario I.

In Scenario II, where decisions are made about individual physical samples, it is possible to widen the required bounds for the standard deviation at any concentration outside the gray region. For example, suppose the upper bound of the gray region (UBGR) is at the action level (AL), the lower bound (LBGR) is set at some concentration below UBGR, and the decision error probabilities α and β are specified. Then the project planners require the probability of a Type I error not to exceed α when the true concentration is at or above UBGR, and they require the probability of a Type II error not to exceed β when the true concentration is at or below LBGR. The decision rule is based on the combined standard uncertainty of the measurement result: any sample whose measured concentration, x, exceeds AL minus $z_{1-\alpha}$ times the combined standard uncertainty, $u_c(x)$, is assumed to exceed the action level. So, assuming $u_c(x)$ is an adequate estimate of the analytical standard deviation, the planners' objectives are met if

$$u_c(x) \le \begin{cases} \dfrac{\text{UBGR} - x}{z_{1-\alpha} + z_{1-\beta}}, & \text{if } x \le \text{LBGR} \\ \dfrac{x - \text{LBGR}}{z_{1-\alpha} + z_{1-\beta}}, & \text{if } x \ge \text{UBGR} \\ \dfrac{\Delta}{z_{1-\alpha} + z_{1-\beta}}, & \text{if LBGR} \le x \le \text{UBGR} \end{cases}$$

EXAMPLE: Consider the earlier example in which AL = UBGR = 1.0 Bq/L, LBGR = 0.5 Bq/L, $\alpha = 0.05$, $\beta = 0.10$, and $u_{MR} = 0.17$ Bq/L. The less restrictive uncertainty requirement can be expressed as

$$u_c(x) \le \begin{cases} \dfrac{1.0 - x}{2.927}, & \text{if } x \le 0.5 \text{ Bq/L} \\ \dfrac{x - 0.5}{2.927}, & \text{if } x \ge 1.0 \text{ Bq/L} \\ 0.17, & \text{if } 0.5 \text{ Bq/L} \le x \le 1.0 \text{ Bq/L} \end{cases}$$

So, if $x = 0$, the requirement is $u_c(x) \le 1 / 2.927 = 0.34$ Bq/L, and, if $x = 2$, the requirement is $u_c(x) \le (2 - 0.5) / 2.927 = 0.51$ Bq/L, which is approximately 26% in relative terms.

C.4.2 Acceptance Criteria for Quality Control Samples

The next issue to be addressed is how to set warning and control limits for quality control (QC) sample results. These limits will be used by project data assessors to determine whether the laboratory appears to be meeting MQOs. Presumably the lab has stricter internal QC requirements (see Chapter 18, *Laboratory Quality Control*).

The development of acceptance criteria for QC samples will be illustrated with an example. Assume the upper bound of the gray region (UBGR) is 5 Bq/kg (soil) and the lower bound of the gray region (LBGR) is 1.5 Bq/kg. The width of the gray region is $\Delta = 5 - 1.5 = 3.5$ Bq/kg. Project planners, following MARLAP's guidance, choose the required method uncertainty at 5 Bq/kg (UBGR) to be

$$u_{MR} = \frac{\Delta}{10} = 0.35 \text{ Bq/kg}$$

or 7%. So, the maximum standard uncertainty at analyte concentrations less than 5 Bq/kg should be $u_{MR} = 0.35$ Bq/kg, and the maximum *relative* standard uncertainty at concentrations greater than 5 Bq/kg should be $\varphi_{MR} = 0.07$, or 7%.

Although it is possible to relax these uncertainty criteria for samples with very high analyte concentrations, MARLAP recommends that the original criteria be used to develop acceptance limits for the results of QC sample analyses.

C.4.2.1 Laboratory Control Samples

It is assumed that the concentration of a laboratory control sample (LCS) is high enough that the relative uncertainty limit $\varphi_{MR} = 0.07$ is appropriate. The *percent deviation* for the LCS analysis is defined as

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

where

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

It is assumed that the uncertainty of SA is negligible; so, the maximum allowable relative standard deviation of $\%D$ is the same as that of the measured result itself, or $\varphi_{MR} \times 100\%$. Then the 2-

sigma warning limits for $\%D$ are $\pm 2\varphi_{MR} \times 100\%$ and the 3-sigma control limits are $\pm 3\varphi_{MR} \times 100\%$. (In situations where φ_{MR} is very small, the uncertainty of SA should not be ignored.)

The requirements for LCSs are summarized below.

Laboratory Control Samples

Statistic: $\%D = \dfrac{SSR - SA}{SA} \times 100\%$

Warning limits: $\pm 2\varphi_{MR} \times 100\%$

Control limits: $\pm 3\varphi_{MR} \times 100\%$

EXAMPLE

(UBGR = 5 Bq/kg, u_{MR} = 0.35 Bq/kg, φ_{MR} = 0.07.)

Suppose an LCS is prepared with a concentration of SA = 10 Bq/kg and the result of the analysis is 11.61 Bq/kg with a combined standard uncertainty of 0.75 Bq/kg. Then

$$\%D = \frac{11.61 - 10}{10} \times 100\% = 16.1\%$$

The warning limits in this case are

$$\pm 2\varphi_{MR} \times 100\% = \pm 14\%$$

and the control limits are

$$\pm 3\varphi_{MR} \times 100\% = \pm 21\%$$

So, the calculated value of $\%D$ is above the upper warning limit but below the control limit.

318 C.4.2.2 Duplicate Analyses

319 Acceptance criteria for duplicate analysis results depend on the sample concentration, which is
320 estimated by the average $\bar{x}$ of the two measured results x_1 and x_2.

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

321 When $\bar{x}$ < UBGR, the warning limit for the absolute difference $|x_1 - x_2|$ is

$$2u_{MR}\sqrt{2} \approx 2.83\, u_{MR}$$

322 and the control limit is

$$3u_{MR}\sqrt{2} \approx 4.24\, u_{MR}$$

323 Only upper limits are used, because the absolute value $|x_1 - x_2|$ is being tested.

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

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

326 The warning limit for RPD is

$$2\varphi_{MR}\sqrt{2} \times 100\% \approx 2.83\, \varphi_{MR} \times 100\%$$

327 and the control limit is

$$3\varphi_{MR}\sqrt{2} \times 100\% \approx 4.24\, \varphi_{MR} \times 100\%$$

328 The requirements for duplicate analyses are summarized below.

Duplicate Analyses

If $\bar{x}$ < UBGR:

Statistic: $|x_1 - x_2|$

Warning limit: $2.83\ u_{MR}$

Control limit: $4.24\ u_{MR}$

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

Statistic: $\text{RPD} = \dfrac{|x_1 - x_2|}{\bar{x}} \times 100\%$

Warning limit: $2.83\ \varphi_{MR} \times 100\%$

Control limit: $4.24\ \varphi_{MR} \times 100\%$

EXAMPLE

(UBGR = 5 Bq/kg, u_{MR} = 0.35 Bq/kg, φ_{MR} = 0.07)

Suppose duplicate analyses are performed on a laboratory sample and the results of the two measurements are

x_1 = 9.0 Bq/kg with combined standard uncertainty $u_c(x_1)$ = 2.0 Bq/kg

x_2 = 13.2 Bq/kg with combined standard uncertainty $u_c(x_2)$ = 2.1 Bq/kg

The duplicate results are evaluated as follows.

$$\bar{x} = \frac{9.0 + 13.2}{2} = 11.1 \text{ Bq/kg}$$

Since $\bar{x} \geq 5$ Bq/kg, the acceptance criteria are expressed in terms of RPD.

$$\text{RPD} = \frac{|9.0 - 13.2|}{11.1} \times 100\% = 37.84\%$$

The warning and control limits for RPD are

$$\text{Warning limit} = 2.83 \times 0.07 \times 100\% = 19.81\%$$
$$\text{Control limit} = 4.24 \times 0.07 \times 100\% = 29.68\%$$

In this case, the value of RPD is above the control limit. (Also note that the relative standard uncertainties are larger than the 7% required for concentrations above 5 Bq/kg.)

C.4.2.3 Method Blanks

Case 1. If an aliquant of blank material is analyzed, or if a nominal aliquant size is used in the data reduction, the measured blank result is an activity concentration. The target value is zero, but the measured value may be either positive or negative. So, the 2-sigma warning limits are $\pm 2u_{MR}$ and the 3-sigma control limits are $\pm 3u_{MR}$.

Case 2. If no blank material is involved (only reagents, tracers, etc., are used), the measured result may be a total activity, not a concentration. In this case the method uncertainty limit u_{MR} should be multiplied by the nominal or typical aliquant size, M_S. Then the 2-sigma warning limits are $\pm 2u_{MR}M_S$ and the 3-sigma control limits are $\pm 3u_{MR}M_S$.

The requirements for method blanks are summarized below.

Method Blanks

Concentration:

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

Total Activity:

Statistic:	Measured total activity
Warning limits:	$\pm 2u_{MR}M_S$
Control limits:	$\pm 3u_{MR}M_S$

EXAMPLE

(UBGR = 5 Bq/kg, u_{MR} = 0.35 Bq/kg, φ_{MR} = 0.07)

Suppose a method blank is analyzed and the result of the measurement is

x = 0.00020 Bq with combined standard uncertainty $u_c(x)$ = 0.00010 Bq

Assuming the nominal aliquant mass is 1.0 g, or M_S = 0.001 kg, the result is evaluated by comparing x to the warning and control limits:

$$\pm 2\,u_{MR}M_S = \pm 0.00070 \text{ Bq}$$
$$\pm 3\,u_{MR}M_S = \pm 0.00105 \text{ Bq}$$

In this case x is within the warning limits.

C.4.2.4 Matrix Spikes

The acceptance criteria for matrix spikes are more complicated than those described above for laboratory control samples because of pre-existing activity in the unspiked sample, which must be measured and subtracted from the activity measured after spiking. The *percent deviation* for a matrix spike is defined as

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

where

SSR is the spiked sample result
SR is the unspiked sample result
SA is the spike concentration added (total activity divided by aliquant mass).

However, warning and control limits for $\%D$ depend on the measured values; so, $\%D$ is not a good statistic to use for matrix spikes. Instead we define a "Z score"

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

where "max(x, y)" denotes the maximum of x and y. Then warning and control limits for Z are set at ± 2 and ± 3, respectively. (It is assumed again that the uncertainty of SA is negligible.) The requirements for matrix spikes are summarized below.

Matrix Spikes

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

Warning limits: ± 2

Control limits: ± 3

EXAMPLE

(UBGR = 5 Bq/kg, u_{MR} = 0.35 Bq/kg, φ_{MR} = 0.07)

Suppose a matrix spike is analyzed. The result of the original (unspiked) analysis is

SR = 3.5 with combined standard uncertainty u_c(SR) = 0.29

the spike concentration added is

SA = 10.1 with combined standard uncertainty u_c(SA) = 0.31

and the result of the analysis of the spiked sample is

SSR = 11.2 with combined standard uncertainty u_c(SSR) = 0.55

Since SR is less than UBGR (5), max(SR, UBGR) = UBGR = 5. So,

$$Z = \frac{SSR - SR - SA}{\varphi_{MR}\sqrt{SSR^2 + UBGR^2}} = \frac{11.2 - 3.5 - 10.1}{0.07\sqrt{11.2^2 + 5^2}} = -2.80$$

So, Z is less than the lower warning limit (–2) but slightly greater than the lower control limit (–3).

C.5 References

Environmental Protection Agency (EPA). 2000. *Guidance for the Data Quality Objectives (DQO) Process*. EPA QA/G-4. EPA/600/R-96/055, EPA, Quality Staff, Washington, DC.

MARSSIM. 2000. *Multi-agency Radiation Survey and Site Investigation Manual* (MARSSIM) Rev. 1. NUREG-1575, Nuclear Regulatory Commission, Washington, DC. EPA 402-R-97-016, Environmental Protection Agency, Washington, DC.

Nuclear Regulatory Commission (NRC). 1998. *A Nonparametric Statistical Methodology for the Design and Analysis of Final Status Decommissioning Surveys*. NUREG-1505. NRC, Washington, DC.

APPENDIX D CONTENT OF PROJECT PLAN DOCUMENTS

D1.0 Introduction

Project plan documents were discussed in Chapter 4, *Project Plan Documents*. This appendix will discuss appropriate content of plan documents. The content of project plan documents, regardless of the document title or format, will include similar information, including the project description and objectives, identification of those involved in the project activities and their responsibilities and authorities, enumeration of the quality control (QC) procedures to be followed, reference to specific standard operating procedures (SOPs) that will be followed for all aspects of the projects, and Health and Safety protocols.

The discussion of project plan document content in this appendix will rely on EPA's guidance on elements for a QA project plan (QAPP). MARLAP selected EPA's QAPP as a model for content of a project plan document since it is closely associated with the data quality objective (DQO) planning process and because other plan documents lack widely accepted guidance regarding content. MARLAP hopes that presentation of a project plan document in one of the most commonly used plan formats will facilitate plan writing by those less familiar with the task, provide a framework for reviewing plan documents, and aid in tracking projects.

The discussion of plan content in sections D2 to D5 follows the outline developed by EPA requirements (EPA, 1998b) and guidance (EPA, 1998a) for QAPPs for environmental data operations. The QAPP elements are presented in four major sections (Table D1) that are referred to as "groups":

- Project Management ;
- Measurement/Data Acquisition;
- Assessment/Oversight; and
- Data Validation and Usability.

There are many formats that can be used to present the project plan elements. MARLAP does not recommend any particular plan format over another. The project planning team should focus on the appropriate content of plan documents needed to address the necessary quality assurance (QA), QC, and other technical activities that must be implemented to ensure that the results of the work performed will satisfy the stated performance criteria. Table D2 provides a crosswalk between the table of contents of two example project plan documents—a QAPP and a work plan—and EPA's (1998a) project plan document elements.

TABLE D1—QAPP Groups and Elements [a,b]

GROUP	ID	ELEMENT	APPENDIX SECTION	MARLAP CHAPTER
A Project Management	A1	Title and Approval Sheet	D2.1	NA
	A2	Table of Contents	D2.2	NA
	A3	Distribution List	D2.3	NA
	A4	Project/Task Organization	D2.4	2
	A5	Problem Definition/Background	D2.5	2
	A6	Project/Task Description	D2.6	2
	A7	Quality Objectives and Criteria for Measurement Data	D2.7	2, 3
	A8	Special Training Requirements/Certifications	D2.8	7
	A9	Documentation and Record	D2.9	7, 17
B Measurement/Data Acquisition	B1	Sampling Process Design	D3.1	NA
	B2	Sample Methods Requirements	D3.2	NA
	B3	Sample Handling and Custody Requirements	D3.3	11
	B4	Analytical Methods Requirements	D3.4	6
	B5	QC Requirements	D3.5	18
	B6	Instrument/Equipment Testing, Inspection and Maintenance Requirements	D3.6	15
	B7	Instrument Calibrations and Frequency	D3.7	18
	B8	Inspection/Acceptance Requirements for Supplies and Consumables	D3.8	NA
	B9	Data Acquisition Requirements (Non-direct Measurements)	D3.9	2
	B10	Data Management	D3.10	17
C Assessment/Oversight	C1	Assessments and Response Actions	D4.1	7
	C2	Reports to Management	D4.2	9
D Data Validation and Usability	D1	Verification and Validation Requirements	D5.1	8
	D2	Verification and Validation Methods	D5.2	8
	D3	Reconciliation with Data Quality Objectives	D5.3	9

(a) Based on EPA, 1998a.

(b) MARLAP recommends a graded approach to project plan documents. All elements may not be applicable, especially for a small project. See Chapter 4, Section 4.3, "A Graded Approach to Project Plan Documents" and Section 4.5.3, "Plan Content for Small Projects."

This appendix also will discuss how the project plan document is linked to the outputs of the project planning process. Directed project planning is discussed in Chapter 2, *Project Planning Process*. The discussion of project plan documents in this appendix will use the DQO process

(EPA, 1994) as a model for directed planning (see Appendix B, *The Data Quality Objectives Process*). References will be made in this appendix to the steps of the DQO process, where appropriate, to illustrate the linkage between the direct planning process and plan documents.

It should be noted that although the project plan documents will address both sampling and analysis, MARLAP does not provide guidance on sampling design issues or sample collection. Discussion in D3.1, "Sample Process Design," and D3.2, "Sample Methods Requirements," are provided for completeness and consistency.

D2.0 Group A: Project Management

This group consists of nine elements that address project management issues such as organization of the plan itself, management systems, and a description of project goals, participants and activities. These elements ensure that the project goals are clearly stated, the approach to be used is understood, and the project planning decisions are documented.

TABLE D2—Comparison of Project Plan Contents

I. Example QAPP[a] using EPA Guidance[b] and EPA QAPP Elements[c]

QA PROJECT PLAN FOR RADIOLOGICAL MONITORING TABLE OF CONTENTS	EPA G-5 QA PROJECT PLAN ELEMENTS
Title Page Approval Sheet Distribution List	A1 Title and Approval Sheet A3 Distribution List
1.0 Table of Contents	A2 Table of Contents
2.0 Project Description 2.1 Site History 2.2 Project Objectives and Requirements 2.3 DQOs	A5 Problem Definition/Background A6 Project/Task Description
3.0 Project Organization and Responsibility	A4 Project/Task Organization
4.0 QA Objectives for Measurement Data (Precision, Accuracy, Representativeness, Comparability, Completeness)	A7 Quality Objectives and Criteria for Measurement Data
5.0 Sampling Procedures, including QC [Cited Field Sampling and Analysis Plan]	B1 Sampling Process Designs B2 Sampling Methods Requirements
6.0 Sample Custody 6.1 Sample 6.2 Sample Identification 6.3 COC Procedures	B3 Sample Handling and Custody Requirements
7.0 Calibration Procedures and Frequency (Field and Laboratory)	B7 Instrument Calibration and Frequency

QA PROJECT PLAN FOR RADIOLOGICAL MONITORING TABLE OF CONTENTS	EPA G-5 QA PROJECT PLAN ELEMENTS
8.0 Analytical Procedures 8.1 Background 8.2 Specific Analytical Procedures 8.3 Test Methods 8.4 Control of Testing 8.5 Limits of Detection	B4 Analytical Methods Requirements B6 Instrument/Equipment Testing, Inspection, and Maintenance Requirements
9.0 Data Reduction, Validation and Reporting and Record	B10 Data Management D1 Data review, Validation, and Verification Requirements A9 Documentation and Records
10.0 Internal QC Checks	B5 Quality Control Requirements
11.0 Performance and Systems Audits 11.1 Systems Audits 11.2 Surveillance 11.3 Performance Audits 11.4 Resolution of Discrepancies 11.5 Review of Contractor Procedures	C1 Assessment and Response Actions
12.0 Preventive Maintenance	B6 Instrument/Equipment Testing, Inspection, and Maintenance Requirements
13.0 Specific Routine Procedures to Assess Data Precision, Accuracy, Completeness	D3 Reconciliation with DQOs
14.0 Corrective Action	
15.0 QA Report to Management	C2 Response to Management
16.0 References	
	A8 Special Training Requirements/Certification
	B8 Inspection/Acceptance Requirements for Supplies and Consumables
	B9 Data Acquisition Requirement for Non-direct Measurements
	D2 Verification and Validation Methods

II. Example Work Plan[d] and EPA QA/G-5 QAPP Elements[e]

Work Plan Table of Contents	EPA QAPP Elements
Cover Letter	A3 Distribution List
Title Page (including Document Number, Prepared by/Prepared for Identification)	A1 Title and Approval Sheet
Approvals	A1 Title and Approval Sheet
Table of Contents	A2 Table of Contents
1 Introduction/Background	
Site and Regulatory Background	A5 Problem Definition/Background

Work Plan Table of Contents	EPA QAPP Elements
Project Scope and Purpose	A6 Project/Task Description
Project Organization and Management	A4 Project/Task Organization
Data Quality Objectives and Approach	A7 Quality Objectives and Criteria for Measurement Data
Environmental Setting	A5 Problem Definition/Background
Sampling Site Selection, Locations and Identification	B1 Sampling Process Design
2 Sampling and Analysis Plan	
Objective	B1 Sampling Process Design
QA Objectives for Field Measurements, Laboratory Measurements (including Calibration Procedures and Frequency)	A7 Quality Objectives and Criteria for Measurement Data B7 Instrument Calibrations and Frequency
Sample Collection Procedures	B2 Sample Methods Requirements
Sample Identification, Handling and Transport	B3 Sample Handling and Custody Requirements
Sample Analysis	B4 Analytical Methods Requirements
Sample Tracking and Records	B10 Data Management
Data Reduction, Validation and Reporting	D1 Data Review, Verification, and Validation Requirements D2 Verification and Validation Methods
Internal QC Checks	B5 QC Requirements
3 QA Project Plan	
QA Training and Awareness	
Performance and Systems Audits	C1 Assessments and Response Actions
Preventive Maintenance	B6 Instrument/Equipment Testing, Inspection, and Maintenance Requirements
Quality Improvement	B6 Instrument/Equipment Testing, Inspection, and Maintenance Requirements
QA Reports to Management	C2 Reports to Management
Purchase Items and Service Control	B8 Inspection/Acceptance Requirements for Supplies and Consumables
4 Data and Records Management Plan Objectives Data Management Document Control Records Management System Administrative Records	A9 Documentation and Record B10 Data Management
5 Data Interpretation Plan Approach for Data Evaluation Data Interpretation and Comparisons	D3 Reconciliation with DQOs
6 Risk Analysis Plan	—
7 Health and Safety Plan	—

Work Plan Table of Contents	EPA QAPP Elements
	B9 Data Acquisition Requirements (Non-direct Measurements)
	A8 Special Training Requirements/Certifications

(a) Plan elements adapted from DOE, 1997.
(b) EPA, 1980.
(c) EPA, 1998a
(d) Plan elements adapted from DOE, 1996.

D2.1 Project Management (A1): Title and Approval Sheet

The project title sheet should:

- Clearly identify the project in an unambiguous manner;
- Include references to organizational identifiers such as project numbers (when appropriate);
- Clearly label and distinguish between draft and approved versions;
- Include the date of issuance of drafts or final approved version;
- Include revision or version numbers;
- Indicate if the document represents only a portion of the QAPP (e.g., Volume 1 of 4 Volumes);
- Include names of the organization(s) preparing the plan document and, if different, for whom the plan was prepared; and
- Identify clearly on the title page if the document is a controlled copy and subjected to no-copying requirements. If so, indicate the document control number.

QAPPs should be reviewed on an established schedule. QAPPs should be kept current and revised when necessary. Documented approval, as an amendment to the QAPP, should be obtained for modifications to the QAPP.

The approval sheet documents that the QAPP has been reviewed and approved prior to implementation. The approval sheet should consist of the name, title, organization, signature and signature date for:

- The project manager or other person with overall responsibility for the project;
- The QA manager or other person with overall responsibility for the quality of the project outputs;
- The project managers or QA managers for all organizations (e.g., sampling organization, laboratories, data validators) implementing project activities; and
- The representative of any oversight or regulatory organization.

The project manager or other person with overall responsibility for the project should require an approved QA program, management plan, or quality manual that supports all technical operations, including data collection and assessment activities.

D2.2 Project Management (A2): Table of Contents

The table of contents should:

- List all sections and subsections of the document, references, glossaries, acronyms and abbreviations, appendices (including sections and subsections) and the associated page numbers;
- List all attachments and the associated page numbers;
- List all tables and associated page numbers;
- List all figures and diagrams and associated page numbers; and
- List titles of other volumes, if the QAPP consists of more than one volume.

A document control format is useful in maintaining reference to the latest version of the planned document, especially when only portions of a document have been copied and are being used to implement or discuss project activities.

D2.3 Project Management (A3): Distribution List

The distribution list should identify all individuals, along with their titles and organizations, who will receive copies and revisions of the approved QAPP and subsequent revisions. Listed

individuals should include, at a minimum, all managers and QA personnel responsible for the implementation and quality of the data collection activities. The project planning team or the core group (see Chapter 2, Section 2.4) should be included on the document distribution list.

D2.4 Project Management (A4): Project/Task Organization

This QAPP element should:

- Identify the individuals and/or organizations participating in the project, as well as contact information (address, telephone number, fax number, e-mail). The stakeholders, data users, decision makers, and technical planning team members, and the person or organization that will be responsible for project implementation, are identified during the directed planning process (Appendix B, *The DQO Process*, Steps 1 and 7).

- Discuss the roles and responsibilities of the individuals and/or organizations that participate in the data collection, including the roles and responsibilities of the data users, decision makers, and QA manager.

- Include an organizational chart clearly showing the relationship, lines of authority and communication, and mechanisms for information exchange among all project participants.

Complex projects may require more than one organizational chart to properly describe the relationships among participants. At times, to clearly detail an organizations responsibilities and communications, a general inter-organizational chart with primary contacts, responsibilities, and communications may need to be accompanied by secondary charts that describe intra-organizational contacts, responsibilities, and lines of communication.

One of the keys to successful projects is communication. The QAPP should identify the point of contact for resolving field and laboratory problems. The QAPP may also summarize the points of contact for dissemination of data to managers, users and the public.

D2.5 Project Management (A5): Problem Definition/Background

The "Problem Definition/Background" element (A5) and the subsequent elements "Project/Task Description" (A6) and "Quality Objectives and Criteria" (A7) constitute the project description. Separating the project description into three elements focuses and encourages the plan authors to address all key issues (identification of problem to be solved, description of site history, description of tasks and the quality objectives and data-acceptance criteria), some of which can

be overlooked if a larger, less-focused section is written. Table D3 provides bulleted components for these three elements. This section and sections D2.6 and D2.7 provide a more detailed discussion of these elements.

TABLE D3—Content of the Three Elements that Constitute the Project Description

Problem Definition/Background (A5)	Project/Task Description (A6)	Objectives and Criteria (A7)
• Serves as an Introduction • Identifies the "problem to be solved" or the "question to be answered" • Identifies the regulatory, legal or "informational needs" drivers • Presents the historical perspective	• Describes measurements • Identifies regulatory standards and action levels • Identifies special personnel, procedural and equipment requirements • Summarizes assessment tools • Details schedule and milestones • Identifies record and report requirements	**Quality Objectives** • Problem definition/Site history • Data inputs • Population boundaries • Tolerable decision error rates **Criteria for Measurement Data** • Measurement quality objectives (MQOs; such as the measurement uncertainty at some concentration; the detection capability; the quantification capability; the range; the specificity; and the ruggedness of the method)

The Problem Definition/Background element provides a discussion of the problem and pertinent background so that the implementation team can understand the context of the project. This section does not discuss the details of project activities, which are described in a subsequent project management element. Much of the information needed for this element was collected and discussed during Step 1 of the DQO process (Appendix B3.1). The decision statement was developed during Step 2 of the DQO process.

The "Problem Definition/Background" element should:

- Serve as an introduction to the project;
- Identify the "problem to be solved" or the "question to be answered" upon successful completion of the project—the decision rule (Appendix B3.6);
- Discuss the assumptions, limitations, and scope of the project;
- Identify the regulatory, legal, or "informational needs" drivers that are the underlying reasons for the project;
- Describe the context of the project so that it can be put into a historical perspective. This section may include a description and maps of a facility or site, its location, its use, site topography, geology and hydrogeology, past data collection activities, historical data including analytes and concentrations, past and present regulatory status, past releases, seriousness and potential risk of any release, site maps, and utilities; and
- If the data collection activity is in support of a technology evaluation, include a discussion of the purpose of the demonstrations, how the technology works, operating conditions, required utilities, effluents and waste by-products and residues, past and expected efficiencies and multi-media mass-balances by analyte and matrix.

D2.6 Project Management (A6): Project/Task Description

This element of the QAPP provides a discussion of the project and underlying tasks for the implementation teams. It should provide a description of the work to be performed to resolve the problem or answer the question, including the following information:

- A description of the measurements and the associated QA/QC procedures that are to be made during the course of the project. DQO Step 3 describes existing and needed data inputs, while Step 7 yields the optimized sampling and analytical designs as well as quality criteria.
  - Identification of the analytes of interest.
  - A summary (preferably a table) of samples type (e.g., grab, spatial or temporal composite), number of samples, analyte or analyte class (e.g., ^{99}Tc, transuranic, gamma emitters) and analytical protocol specifications or method.
- A discussion of applicable regulatory standards or action levels to which measurements will be compared. Identify any applicable regulatory standard (e.g., gross alpha drinking water maximum contamination limit), or applicable or relevant and appropriate requirements

(ARARs) that will be used as a metric or action level during decision-making. The DQO Step 6 details action levels and tolerable decision errors that will be the basis for decisions.

- Identify any special requirements required to implement project tasks.
  - Identify any special training (e.g., hazardous waste site health and safety training (29 CFR 1910.120), radiation safety training).
  - Identify any special protective clothing and sampling equipment.
  - Identify any boundary conditions (e.g., only sample after a rainfall of more than 1 inch).
  - Specify any special document format, chain-of-custody, or archival procedures.
  - Identify any special sample handling (e.g., freezing of tissue samples), instrumentation, or non-routine analytical protocols that are required to achieve specified performance criteria (e.g., very low detection limits) (see also Chapter 3, *Critical Analytical Planning Issues and Developing Analytical Protocol Specifications*).

- Summarize the assessment tools that will be employed to determine whether measurement data complied with performance criteria and are suitable to support decision-making. Include a schedule of the assessment events. Assessment tools include performance evaluations, program technical reviews, surveillance, technical and systems audits, and verification and validation. Briefly outline:
  - A first tier of reviews (e.g., when field or lab personnel check each other's notes or calculations).
  - Reviews of the work, notes and calculations of subordinates by the supervisor (e.g., review and sign all notebook entries).
  - The percentage of data subject to review by internal QA staff.
  - Data verification and validation to be performed by an independent party and the guidelines or plan to be used.
  - Assessment of project activities to be conducted by personnel independent of project activities (e.g., performance evaluation samples, surveillance, audits).
  - Assessment of how results of the project will be reconciled with the project DQOs ("data quality assessment").

- Supply a schedule that includes start and completion dates for tasks and a list of completion dates for important milestones. Dates can be calendric, or as number of days following approval of the QAPP, or number of days following commencement of field operations. DQO Steps 1 and 4 identify deadlines and other constraints that can impact scheduling.

- Identify the records and reports that will be required. This should be a brief but complete listing of necessary reports and records (e.g., field and lab notebooks, sample logbooks,

spectra, sample tracking records, laboratory information system print-outs, QA reports, corrective action reports).

- Identify whether the original documents are required or if photocopies are sufficient. More detailed information will be presented in "Documentation and Records" (A9) and "Data Management" (B10).

D2.7 Project Management (A7): Quality Objectives and Criteria for Measurement Data

This element addresses two closely related but different issues, quality objectives for the project and criteria used to evaluate the quality of measurement data. The element summarizes outputs from all steps of the DQO process. A fundamental principle underlying plan documents is that requirements for the data quality must be specified by the project planning team and documented. By clearly stating the intended use of the data and specifying qualitative and quantitative criteria for system performance, a critical link between the needs of the project planning team and the performance requirements to be placed on the laboratory data is established. (See Chapter 3 for a discussion of MQOs.)

D2.7.1 Project's Quality Objectives

The project's quality objectives or data quality objectives (DQOs) are qualitative and quantitative statements that:

- Clarify the intended use of the data (e.g., data will be used to determine if lagoon sediment contains ^{232}Th at concentrations greater than or equal to the action level);

- Define the type and quantity of data per matrix needed to support the decision (e.g., ^{232}Th concentrations in 300 composite sediments samples each composite consisting of 10 samples randomly collected from a 100 m^2 sampling grid adjacent to the point of discharge);

- Identify the conditions under which the data should be collected (e.g., sediment samples collected from the top 6 cm of sediment within a 100 m radius of the point of discharge into lagoon #1, following de-watering of the lagoon and prior to sediment removal); and

- Specify tolerable limits on the probability of making a decision error due to uncertainty in the data and any associated action levels (e.g., 95 percent confidence that the true concentration is actually below the action level).

Authors of project plan documents are often encouraged to condense the DQO outputs in a summary statement. This approach can have value as long as critical information is not lost in the summary process and the original information is cited and available for all project participants. The following is an example of a DQO summary statement:

> "The purpose of this project is to determine, to within a lateral distance of 10 m, the extent of ^{232}Th in soil along a pipeline at concentrations at or above 1,145 mBq/g, with a false positive rate less than or equal to 5 percent; and to define within 1 m the vertical extent of measured ^{232}Th concentrations greater than 7,400 mBq/g."

D2.7.2 Specifying Measurement Quality Objectives

Measurement quality objectives (MQOs) or measurements performance criteria are essential to the success of a project since they establish the necessary quality of the data. The quality of data can vary as a result of the occurrence and magnitude of three different types of errors (Taylor, 1990).

- BLUNDERS—mistakes that occur on occasion and produce erroneous results (e.g., mis-labeling or transcription errors);
- SYSTEMATIC ERRORS—mistakes that are always the same sign and magnitude and produce bias (i.e., they are constant no matter how many measurements are made); and
- RANDOM ERRORS—mistakes that vary in sign and magnitude and are unpredictable on an individual basis (i.e., random differences between repetitive readings) but will average out if enough measurements are taken.

The frequent occurrence of these types of errors is the reason why data quality is subject to question, why there is uncertainty when using data to make decisions and why measurement performance criteria are necessary.

During the DQO process, project DQOs are used to establish the MQOs. An MQO is a statement of a performance objective or requirement for a particular method performance characteristic. Examples of method performance characteristics include the measurement uncertainty at some concentration; the detection capability; the quantification capability; the range; the specificity; and the ruggedness of the method. MQOs for the project should be identified and described within this element of the QAPP. MARLAP provides guidance for developing MQOs for select method performance characteristics in Chapter 3 and Appendix C.

D2.7.3 Relation between the Project DQOs, MQOs, and QC Requirements

The ultimate goal of all data collection operations is the collection of appropriately accurate data. Appropriately accurate data are data for which errors caused by imprecision and bias are controlled such that it is suitable for use in the context outlined by the DQOs (i.e., the overall error is less than that specified in the acceptable decision error). During the optimization of design in the planning process, DQO-specified decision error rates are translated into MQOs with the intention of monitoring, detecting, quantifying and controlling imprecision and analytical bias. During optimization, precautions are also incorporated into the design with the intention of preventing blunders and types of non-measurable bias not susceptible to measurement by QC samples.

The MQOs provide acceptance or rejection criteria for the quality control samples whose types and frequency are discussed in the Quality Control Requirements element (B5) (Appendix C). QC samples and the project's associated MQOs are key—but not the sole mechanisms—for monitoring the achievement of DQOs.

In summary, translating acceptable decision error rates into a design that will produce data of appropriate precision and bias is often a complex undertaking. The team must consider the synergistic and antagonistic interactions of the different options for managing errors and uncertainty. Accurate data require not only control of imprecision, but must also control the various forms of bias.

D2.8 Project Management (A8): Special Training Requirements/Certification

All project personnel should be qualified and experienced in their assigned task(s). The purpose of this element is to add additional information regarding special training requirements and how they will be managed during implementation of the project. This element should:

- Identify and describe any mandated or specialized training or certifications that are required;
- Indicate if training records or certificates are included in the QAPP as attachments;
- Explain how training will be implemented and certifications obtained; and
- Identify how training documentation and certification records will be maintained.

D2.9 Project Management (A9): Documentation and Record

This element of the QAPP will identify which records are critical to the project, from data generation in the field to final use. It should include what information needs to be contained in

these records and reports, the formats of the records and reports, and a brief description of document control procedures. The following are suggested records and content:

- SAMPLE COLLECTION RECORDS should include sampling procedures, the names of the persons conducting the activity, sample number, sample collection points, maps and diagrams, equipment/protocol used, climatic conditions, and unusual observations. Bound field notebooks, pre-printed forms, or computerized notebooks can serve as the recording media. Bound field notebooks are generally used to record raw data and make references to prescribed procedures, changes in planned activities and implementation of corrective actions. Preferably, notebooks will contain pre-numbered pages with date and signature lines and entries will be made in ink. Field QC issues such as field, trip, and equipment rinsate blanks, co-located samples, field-spiked samples, and sample preservation should be documented. Telephone logbooks and air bill records should be maintained.

- SAMPLE TRACKING RECORDS document the progression of samples as they travel from the original sampling location to the laboratory and finally to their disposal or archival. These records should contain sample identification, the project name, signatures of the sample collector, the laboratory custodian and other custodians, and the date and time of receipt. The records should document any sample anomalies. If chain-of-custody (COC) is required for the project, the procedures and requirements should be outlined (Chapter 11, *Sample Receipt, Inspection and Tracking*).

- ANALYTICAL QC issues that should be documented include standard traceability, and frequency and results of QC samples, such as, method and instrument blanks, spiked samples, replicates, calibration check standards and detection limit studies.

- ANALYTICAL RECORDS should include standard operating procedures for sample receipt, preparation, analysis and report generation. Data report formats and the level of supporting information is determined by data use and data assessment needs.

- PROJECT ASSESSMENT RECORDS should include audit check lists and reports, performance evaluation (PE) sample results, data verification and validation reports, corrective action reports. The project may want to maintain copies of the laboratory proposal package, pre-award documentation, initial precision and bias test of the analytical protocol and any corrective action reports.

The QAPP should indicate who is responsible for creating, tracking, and maintaining these records and when records can be discarded, as well as any special requirements for computer, microfiche, and paper records.

D3.0 Group B: Measurement/Data Acquisition

The Measurement/Data Acquisition group consists of 10 elements that address the actual data collection activities related to sampling, sample handling, sample analysis and the generation of data reports. Although these issues may have been previously considered by project management elements, the project management section of the QAPP dealt with the overall perspective. The measurement/data section contains the details covering design and implementation to ensure that appropriate protocols are employed and documented. This section also addresses quality control activities that will be performed during each phase of data collection from sampling to data reporting.

D3.1 Measurement/Data Acquisition (B1): Sampling Process Design

This element of the QAPP describes the finalized sampling design that will be used to collect samples in support of project objectives. The design should describe the matrices to be sampled, where the samples will be taken, the number of samples to be taken, and the sampling frequency. A map of the sampling locations should be included to provide unequivocal sample location determination and documentation.

If a separate sampling and analysis plan or a field sampling and analysis plan has been developed, it can be included by citation or as an appendix. This element will not address the details of standard operating procedures for sample collection, which will be covered in subsequent elements. This element will describe the sampling design and the underlying logic, so that implementation teams can understand the rationale behind and better implement the sampling effort. Understanding the rationale for the decisions will help if plans have to be modified due to conditions in the field. DQO Step 7 establishes the rationale for and the details of the sampling design.

This element should restate the outputs of the planning process and any other considerations and assumptions that impacted the design of the sampling plan, such as:

- The number of samples, including QC samples, sample locations and schedule, and rationale for the number and location of samples;

- A brief discussion of how the sampling design will facilitate the achievement of project objectives;

- A discussion of the population boundaries (temporal and spatial) and any accessibility limitations;

- A description of how the sampling design accommodates potential problems caused by the physical properties of the material being sampled (e.g., large particle size), the characteristic of concern (e.g., potential losses due to the volatility of tritium) or heterogeneity;

- A discussion of the overarching approach to sampling design (e.g., worse case or best case sampling versus average value) and assumptions made in selecting this approach (e.g., an assumption that the darkened soil adjacent to the leaking tank would present a worse case estimate of soil contamination);

- A listing of guidance and references that were relied upon when designing the sampling plan;

- Identification of the characteristics of interest (e.g., ^{99}Tc activity), associated statistical parameters (e.g., mean, standard deviations, 99th percentile), and acceptable false error rates (e.g., false negative rate of less than 5%);

- Identification of relevant action level and how data will be compared to the action level (Appendix B3.2);

- A discussion of the anticipated range of the characteristic of interest and assumed temporal and spatial variations (heterogeneity), anticipated variance, anticipated sources and magnitude of error (e.g., heterogeneity of material being sampled, sampling imprecision, analytical imprecision), anticipated mean values and distribution of measurements and the basis (e.g., historical data, similar processes or sites) for any associated assumptions;

- If any level of bias is assumed, what is the assumed magnitude and the basis of the assumption (e.g., historical data, typical analytical bias for matrix type);

- It is usually assumed that the magnitude of measurements made at individual sampling locations are independent of each other (e.g., no correlation of concentration with location). Geostatistical approaches may be more appropriate if measurements are significantly correlated with locations (e.g., serial-correlation, auto-correlation) since serial-correlation can

bias estimates of variance and invalidate traditional probabilistic techniques such as hypothesis testing; and

- A discussion of the rationale for choosing non-routine sampling protocols and why these non-routine protocols are expected to produce acceptable precision and bias.

D3.2 Measurement/Data Acquisition (B2): Sampling Methods Requirements

This element of the QAPP describes the detailed sampling procedures that will be employed during the project. The preliminary details of sampling methods to be employed were established during Step 7 of the DQO process. The selected sampling procedures should be appropriate to (1) ensure that a representative sample is collected, (2) avoid the introduction of contamination during collection, and (3) properly preserve the sample to meet project objectives. Written SOPs should be included as attachments to the QAPP. This element and the appendices or other documents that it references should in total contain all the project specific details needed to successfully implement the sampling effort as planned. If documents to be cited in the QAPP are not readily available to all project participants, they must be incorporated as appendices. All sampling personnel should sign that they have read the sampling procedures and the health and safety procedures.

Correct sampling procedures and equipment used in conjunction with a correct sampling design should result in a collection of samples that in total will represent the population of interest. A detailed discussion of sampling procedures, equipment and design are beyond the scope of MARLAP. In general, the selected procedures must be designed to ensure that the equipment is used properly and that the collected samples represent the individual sampling unit from which samples are collected. The sampling equipment should be chemically and physically compatible with the analyte of concern as well as the sample matrix. The sampling design should facilitate access to individual sampling units, result in an appropriate mass/volume of sample such that it meets or exceeds minimum analytical sample sizes, accommodates short-range heterogeneity (*i.e.*, does not preclude large particle sizes or lose small particles) and reduce or prevent loss of volatile components, if appropriate.

This element of the QAPP should:

- Identify the sampling methods to be used for each matrix, including the method number if a standardized method. If methods are to be implemented differently than specified by the standard method or if the standard method offers alternatives for implementation, the differences and alternatives should be specified;

- Identify the performance requirements of the sampling method. If the sampling method of choice is unlikely to be able to achieve the level of performance demanded by the project DQO, the project planning team should be notified;

- Identify the required field QC samples (e.g., trip blank, co-located duplicate);

- Identify any sample equipment preparation (e.g., sharpening of cutting edges, degreasing and cleaning) or site preparation (e.g., removal of overburden, establishing dust-free work space for filtering) for each method;

- Identify and preferably generate a list of equipment and supplies needed. For example, the sampling devices, decontamination equipment, sampling containers, consumables (e.g., paper towels), chain-of-custody seals and forms, shipping materials (e.g., bubble-pack, tape), safety equipment and paper work (e.g., pens, field books);

- Identify and detail logistical procedures for deployment, sample shipment and demobilization. If a mobile lab will be used, explain its role and the procedures for sample flow to the mobile lab and data flow to the data-user;

- Identify, preferably in a tabular form, sample container types, sizes, preservatives, and holding times;

- Identify procedures that address and correct problems encountered in the field (variances and nonconformance to the established sampling procedures);

- Identify for each sampling method, decontamination procedures and the procedures for disposing of contaminated equipment and used-decontamination chemicals and waters;

- Identify the disposal procedures for waste residuals generated during the sampling process (e.g., purged well waters, drilling dregs) for each method; and

- Identify oversight procedures (e.g., audits, supervisor review) that ensure that sampling procedures are implemented properly. The person responsible for implementing corrective actions should be identified.

D3.3 Measurement/Data Acquisition (B3): Sample Handling and Custody Requirements

This element of the QAPP details how sample integrity will be maintained and how the sample history and its custody will be documented ensuring that (1) samples are collected, transferred, stored, and analyzed by authorized personnel, (2) the physical, chemical and legal integrity of samples is maintained, and (3) an accurate written record of the history of custody is maintained. DQO Step 1 describes the regulatory situation which can be used to identify the appropriate level of sample tracking. The QAPP should state whether COC is required. Sample handling, tracking and COC requirements are discussed in detail in Chapter 11, *Sample Receipt and Tracking*.

In the QAPP, the following elements should be documented:

- INTEGRITY OF SAMPLE CONTAINERS: Describe records to be maintained on the integrity of sample container and shipping container seals upon receipt. Describe records to be maintained if specially prepared or pre-cleaned containers are required.

- SECURITY: If wells are being sampled, whether the wellheads were locked or unlocked should be noted. Security of remote sampling sites or automatic samplers not maintained in locked cages should be discussed.

- SAMPLE IDENTIFICATION: The assignment of sample numbers and the labeling of sample containers is explained. If samples are to be assigned coded sample identifications (IDs) to preclude the possibility of bias during analysis, the sample code is one of the few items that will not be included in the QAPP, since the lab will receive a copy. The code and sample ID assignment process will have to be described in a separate document, which is made available to the field team and the data validators. An example of a sample label should be included in the QAPP.

- TRACKING OR CUSTODY IN THE FIELD: Procedures for sample tracking or custody while in the field and during sample shipment should be described. When COC is required, a copy of the COC form and directions for completion should be included. A list of all materials needed for tracking or custody procedures should be provided (e.g., bound notebooks, shipping containers, shipping labels, tape, custody seals, COC forms).

- SAMPLE PRESERVATION: Sample preservation procedures, if desired, should be clearly described. Preservation of radiological samples is discussed in Chapter 10, *Requirements When Collecting, Preserving, and Shipping Samples That Require Analytical Measurement.*

- TRACKING OR CUSTODY IN THE LABORATORY: A decision must be made as to whether the laboratory in general is considered a secure area such that further security is not required once the sample is officially received by the laboratory or whether internal tracking or custody procedures will be required as the samples are handled by different personnel within the lab. The laboratory's sample receipt SOP, laboratory security procedures, and—if needed—internal tracking or custody procedures should be described.

- SPECIAL REQUIREMENT: Any special requirements, such as shipping of flammable or toxic samples, or requirements for verification of sample preservation upon sample receipt by the laboratory should be clearly described.

- ARCHIVAL: Document the rationale for the request to archive samples, extracts, and digestates. Describe how samples, extracts, and digestates will be archived. Identify how long samples, extracts, digestates, reports, and supporting documentation must be maintained.

D3.4 Measurement/Data Acquisition (B4): Analytical Methods Requirements

This element of the QAPP should identify the Analytical Protocol Specifications (APSs) including the MQOs that were employed by the laboratory to select the analytical protocols. (See Chapter 3 for guidance on developing APs.) This element integrates decisions from three DQO steps: Step 3 which identified the analyte of interest and needed inputs to the decision, Step 6 which identifies the allowable uncertainty, and Step 7 which identifies the optimized analytical design. Input from all three steps drive the choice of analytical protocols. The discussion of the selected analytical protocols should address: subsampling, sample preparation, sample clean-up, radiochemical separations, the measurement system, confirmatory analyses and pertinent data calculation and reporting issues. A tabular summary of the analytical protocol by matrix type can facilitate reference for both the plan document development team and the laboratory analytical team.

This element of the QAPP should clearly describe the expected sample matrices (e.g., groundwater with no sediments, soils with no rocks larger than 2 cm in diameter) and what should be done or who should be contacted if sample matrices are different than expected. Subsampling is a key link in the analytical process which is often overlooked during planning leaving important decisions to laboratory staff, this element should specify appropriate subsampling procedures.

This QAPP element should:

- Identify the laboratories supplying analytical support. If more than one laboratory will be used, detail the analyses supplied by each laboratory;

- Identify analyses to be performed in the field using portable equipment or by a mobile lab;

- Identify the sample preparation techniques. Non-routine preparatory protocols, such as novel radiochemical separations, should be described in detail and documented in an SOP including pertinent literature citations and the results of validations studies and other performance data, when they exist;

- Identify the analytical protocols to be used. The protocol documentation should describe all necessary steps including the necessary reagents, apparatus and equipment, standards preparation, calibration, sample introduction, data calculation, quality control, interferences, and waste disposal;

- If the selected analytical protocols have not been demonstrated for the intended application, the QAPP should include information about the intended procedure, how it will be validated, and what criteria must be met before it is accepted for the project's application (Chapter 6, *Selection and Application of an Analytical Protocol*);

- If potential analytical protocols were not identified during the project planning process and existing analytical protocols can not meet the MQOs, an analytical protocol will have to be developed and validated (Chapter 6, Section 6.5, "Method Validation"). If this issue was not identified by the project planning team, the project planning team must be contacted because the original project objectives and the associated MQOs may have to be revisited and changed (Appendix B);

- If both high concentration and low concentration samples are expected, discuss how the two sample types will be identified and handled in a manner that will prevent cross-contamination or other analytical problems;

- Discuss reporting requirements (e.g., suitable data acquisition and print-outs or electronic data archival that will capture all necessary information), the proper units (dry weight versus wet weight), the method to be employed to report the final result and its uncertainty, and reporting package format requirements; and

- Identify oversight procedures (e.g., QC samples, audits, supervisor review) for ensuring that analytical procedures are implemented properly and procedures for correcting problems

encountered in the laboratory. The person responsible for implementing corrective actions in the lab should be identified.

The project plan document should be a dynamic document, used and updated over the life of the project as information becomes available or changes. For example, under a performance based approach, the analytical protocols requirements in the project plan documents should initially reflect the Analytical Protocol Specifications established by the project planning team and issued in the statement of work (or task order). When the analytical laboratory has been selected (Appendix E, *Contracting Analytical Services*) the project plan document should be updated to reflect the identification of the selected laboratory and the analytical protocols, that is, the actual analytical protocols to be used should be included by citation or inclusion of the SOPs as appendices.

D3.5 Measurement/Data Acquisition (B5): Quality Control Requirements

This element of the QAPP should include enough detail that the use and evaluation of QC sample results and corrective actions will be performed as planned and support project activities. The QC acceptance limits and the required corrective actions for non-conformances should be described. DQO Step 7 identified the optimized analytical design and the desired MQOs which will help determine the QC acceptance criteria. Refer to Chapter 19.8.1 for information on control charts and Chapter 18, *Quality Assurance and Quality Control*, for a detailed discussion of radioassay QC and quality indicators. A discussion of QC requirements in the QAPP should include the following information:

- A list of all QC sample types by matrix;
- The frequency of QC sample collection or analysis, preferably a tabular listing;
- A list of QC sample acceptance criteria or warning limits and control limits;
- Procedures for documenting QC sample results;
- Equations and calculations used to evaluate QC sample results and to determine measurement performance acceptability;
- Actions to be taken if QC samples fail to meet the acceptance criteria; and
- Identification of the appropriate responsible person to whom QC reports should be sent.

Acceptance criteria for QC samples should be based on the project MQOs, in particular the MQO for measurement uncertainty at some concentration. Appendix C provides guidance on developing acceptance criteria for QC samples based on the project's MQO for the method's measurement uncertainty at some concentration, typically the action level.

D3.6 Measurement/Data Acquisition (B6): Instrument/Equipment Testing, Inspection, and Maintenance Requirements

The QAPP should include a discussion of testing, inspection and maintenance requirements that will be followed to ensure that equipment and instrumentation will be in working order during implementation of project activities. An instrument or testing equipment will be deemed to be in working order if it is maintained according to protocol and it has been inspected and tested and meets acceptance criteria.

This element of the QAPP should:

- Discuss the maintenance policy for all essential instrumentation and equipment, what it involves, its frequency, whether it is performed by internal staff or if it is a contracted service, and whether an inventory of spare parts is maintained;

- Describe the inspection protocols for instrumentation and equipment. This ranges from the routine inspections (i.e, gases, nebulizers, syringes and tubing) prior to instrument or equipment use and more detailed inspections employed while troubleshooting an instrument or equipment problem. Mandatory inspection hold points, beyond which work may not proceed, should be identified; and

- Address the frequency and details of equipment and instrument testing. This may involve the weighing of volumes to test automatic diluters or pipets, the use of a standard weight prior to weighing sample aliquots to the use of standards to test sophisticated instrumentation. If standards (e.g., National Institute of Standards and Technology [NIST] standard reference material [SRM]) are used during testing, the type, source and uncertainty of standard should be identified.

There is not always a clear distinction between the testing component of this element and the previous element addressing the use of QC samples to determine whether an instrument is within control. In any case, it is important to describe in either of these elements of the QAPP, all

procedures that are deemed important to determining whether an instrument/equipment is in working order and within control.

D3.7 Measurement/Data Acquisition (B7): Instrument Calibration and Frequency

This element of the QAPP details the calibration procedures including standards, frequencies, evaluation, corrective action measures and documentation. Summary tables may be used to complement the more detailed discussions in the text. The following issues should be addressed in this element:

- Identify all tools, gauges, sampling devices, instruments, and test equipment that require calibration to maintain acceptable performance;
- Describe the calibration procedures in enough detail in this element or by citation to readily available references so that the calibration can be performed as intended;
- Identify reference equipment (e.g., NIST thermometers) and standards, their sources, and how they are traceable to national standards. Where national standards are not available, describe the procedures used to document the acceptability of the calibration standard used;
- Identify the frequency of calibration and any conditions (e.g., failed continuing calibration standard, power failure) that may be cause for unscheduled calibration;
- Identify the procedure and the acceptance criteria (i.e., in control) to be used to evaluate the calibration data;
- Identify the corrective actions to be taken if the calibration is not in control. When calibration is out of control, describe the evaluations to be made to determine the validity and acceptability of measurements performed since the last calibration; and
- Identify how calibration data will be documented, archived and traceable to the correct instrument/equipment.

See Chapter 16, *Instrument Calibration and Test Source Preparation*, for a discussion of radiochemical instrument calibration.

D3.8 Measurement/Data Acquisition (B8): Inspection/Acceptance Requirements for Supplies and Consumables

This element of the QAPP deals with inspecting and accepting all supplies and consumables that may directly or indirectly affect the quality of the data. For some projects, this information may be provided by citation to a chemical safety and hygiene plan. The contents of this element should contain enough supportive information that the project and the data will be sufficient to undergo solicited and unsolicited reviews. The following detail should be included in this element, so the inspection process can be accurately implemented:

- Identify and document all supplies and consumables (e.g., acids, solvents, preservatives, containers, reagents, standards) that have the potential of directly or indirectly impacting the quality of the data collection activity;

- Identify the significant criteria that should be used when choosing supplies and consumables (e.g., grade, purity, activity, concentration, certification);

- Describe the inspection and acceptance procedures that will be used for supplies or consumables, including who is responsible for inspection, the timing of inspections and the acceptance and rejection criteria. This description should be complete enough to allow replication of the inspection process. Standards for receiving radiological packages are provided in 10 CFR 20 Section 20.1906 "Procedures for Receiving and Opening Packages" or an Agreement State equivalent;

- Describe the procedures for checking the accuracy of newly purchased standards, other than SRMs, by comparison to other standards purchased from other sources;

- Identify any special handling and storage (e.g., refrigerated, in the dark, separate from high concentration standards, lead shielding) conditions that must be maintained;

- Describe the method of labeling, dating and tracking supplies and consumables and the disposal method for when their useful life has expired; and

- Describe the procedures and indicate by job function who is responsible for documenting the inspection process and the status of inventories.

D3.9 Measurement/Data Acquisition (B9): Data Acquisition Requirements for Non-Direct Measurement Data

This element of the QAPP addresses the use of existing data. Non-direct measurement data is defined as existing data that is independent of the data generated by the current project's sampling and analytical activities. Non-direct data may be of the same type (e.g., mBq/g of ^{232}Th in soil) that will complement the data being collected during the project. Other non-direct data may be of a different type such as weather information from the National Weather Service, or geological and hydrogeological data from the U.S. Geological Survey.

To achieve project objectives it is important that the data obtained from non-direct sources be subjected to scrutiny prior to acceptance and use. Use of existing data is discussed during Step 1 and 3 of the DQO process. If existing data of the same type is to be used to achieve project objectives, it has to be evaluated in terms of its ability to comply with MQOs established in DQO Step 7. The limitations on the use of non-direct measurements should be established by the project planning team.

This element should:

- Identify the type and source of all non-direct data that will be needed to achieve the project objectives;
- State whether the same quality criteria and QC sample criteria will be applied to the non-direct measurement data. If the same criteria cannot be applied, then identify criteria that will be acceptable for the non-direct data but at the same time won't bias or significantly add to the uncertainty of decisions for the project;
- Identify whether the data will support qualitative decisions (e.g., rain occurred on the third day of sampling) or if the data will be used quantitatively (e.g., used to calculate a mean concentration that will be compared to an action level);
- Identify whether enough information exists to evaluate the quality of the non-direct data (e.g., spike and collocated sample data, minimum detectable concentrations, reported measurement uncertainties); and
- If the non-direct data are to be combined with project-collected data, identify the criteria that will be used to determine if the non-direct data are comparable (e.g., sampled the same population, same protocol).

D3.10 Measurement/Data Acquisition (B10): Data Management

This element of the QAPP should present an overview of the data management process from the receipt of raw data to data storage. The overview should address all interim steps, such as, data transformations, transmittals, calculations, verifications, validations and data quality assessments. The procedures should address how internal checks for errors are made. Laboratories should follow accepted data management practices (EPA, 1995). Applicable SOPs should be included as attachments to the QAPP. (See Chapter 17, *Data Generation, Reduction and Reporting* for a discussion of radiochemical data generation and reduction.)

The discussion of data management should address the following issues:

- DATA RECORDING: The process of the initial data recording steps (e.g., field notebooks, instrument printouts, electronic data storage of alpha and gamma spectra) should be described. Examples of unique forms or procedures should be described. Describe the procedures to be used to record final results (e.g., negative counts) and the uncertainty.

- CONVERSIONS AND TRANSFORMATIONS: All data conversions (e.g., dry weight to wet weight), transformations (conversion to logs to facilitate data analysis) and calculation of statistical parameters (e.g., uncertainties) should be described, including equations and the rationale for the conversions, transformations and calculations. Computer manipulation of data should be specified (e.g., software package, macros).

- DATA TRANSMITTALS: Data transmittals occur when data are sent to another location or person or when it is converted to another format (incorporated into a spreadsheet) or media (hardcopy reports keyed into a computer database). All transmittals and associated QA/QC steps taken to minimize transcription errors should be described in enough detail to ensure their proper implementation.

- DATA REDUCTIONS: Identify and explain the reasons for data reductions. Data reduction is the process of changing the number of data items by arithmetic or statistical calculations, standard curves, or concentration factors. A laboratory information management system may use a dilution factor or concentration factor to change raw data. These changes often are irreversible and in the process the original data are lost.

- DATA VERIFICATION, VALIDATION AND ASSESSMENTS: Since these assessment issues are discussed in a subsequent element of the QAPP (D2), only an overview should be provided identify the timing and frequency of these assessments.

- DATA TRACKING, STORAGE AND RETRIEVAL: Describe the system for tracking and compiling data as samples are being analyzed, how data are stored, and the mechanism for retrieving data (e.g., from archived back-up tapes or disks).

- SECURITY: Describe procedures for data and computer security.

D4.0 Group C: Assessment/Oversight

The elements of this group are intended to assess progress during the project, facilitate corrective actions in a timely manner (Section D4.1), and provide reports to management (Section D4.2). It should be stressed that early detection of problems and weaknesses—before project commencement or soon thereafter—and initiation of corrective actions are important for a project's success. The focus of the elements in this group is the implementation of the project as defined in the QAPP. This group is different from the subsequent group, data validation and usability, which will assesses project data after the data collection activity is complete.

D4.1 Assessment/Oversight (C1): Assessment and Response Actions

The QAPP authors have a range of assessment choices that can be employed to evaluate on-going project activities, which include surveillance, peer review, systems reviews, technical systems audits (of field and laboratory operations), and performance evaluations. A detailed discussion of laboratory evaluation is presented in Chapter 7, *Evaluating Radiological Laboratories*. It is important to schedule assessments in a timely manner. An assessment has less value if its findings become available after completion of the activity. The goal is to uncover problems and weaknesses before project commencement or soon thereafter and initiate corrective actions so the project is a success.

This element of the QAPP should:

- Identify all assessments by type, frequency and schedule;
- Identify the personnel who will implement the assessments;
- Identify the criteria, documents, and plans upon which assessments will base their review;
- Describe the format of assessment reports;
- Identify the time frame for providing the corrective action plan; and

- Identify who is responsible for approving corrective actions and ensuring that they are implemented.

D4.2 Assessment/Oversight (C2): Reports To Management

Reports to management are a mechanism for focusing management's attention on project quality and on project issues that may require the management's level of authority. To be effective reports to management and management's review and response must be timely. The benefit of these status reports is the opportunity to alert management of data quality problems, propose viable solutions and procure additional resources.

At the end of the project, a final project report which includes the documentation of the DQA findings should be prepared (Chapter 9, *Data Quality Assessment*). It may also be beneficial for future planning efforts for the project planning team to provide a summary of the "lesson learned" during the project, such as key issues not addressed during planning and discovered in implementation or assessment, specialist expertise needed on the planning team, experience with implementing performance-based analytical protocol selection.

This element of the QAPP should address the following issues:

- Identify the various project reports that will be sent to management;
- Identify non-project reports that may discuss issues pertinent to the project (e.g., backlog reports);
- Identify QA reports that provide documentary evidence of quality (e.g., results of independent performance testing, routine QC monitoring of system performance);
- Identify the content of "reports to management" (e.g., project status, deviations from the QAPP and approved amendments, results of assessments, problems, suggested corrective actions, status on past corrective actions);
- Identify the frequency and schedule for reports to management;
- Identify the organization or personnel who are responsible for authoring reports; and
- Identify the management personnel who will receive and act upon the assessment reports.

D5.0 Group D: Data Validation and Usability

This group of elements ensures that individual data elements conform to the project specific criteria. This section of the QAPP discusses data verification, data validation and data quality assessment (DQA), three processes employed to accept, reject or qualify data in an objective and consistent manner. Although there is good agreement as to the range of issues that the three elements, in total, should address, within the environmental community there are significant differences as to how verification, validation and DQA are defined. The discussion of this group of elements will use the definitions which are defined Chapter 8, *Radiochemical Data Verification and Validation.*

D5.1 Data Validation and Usability (D1): Verification and Validation Requirements

This element of the QAPP addresses requirements for both data verification and data validation. The purpose of this element is to clearly state the criteria for deciding the degree to which each data item and the data set as a whole has met the quality specifications described in the "Measurement/Data Acquisition" section of the QAPP. The strength of the conclusions that can be drawn from the data is directly related to compliance with and deviations from the sampling and analytical design. The requirements can be presented in tabular or narrative form.

Verification procedures and criteria should be established prior to the data evaluation. Requirements for data verification include the following criteria:

- Criteria for determining if specified protocols were employed (e.g., compliance with essential procedural steps);
- Criteria for determining if methods were in control (e.g., QC acceptance criteria);
- Criteria for determining if a data report is complete (e.g., list of critical components that constitute the report);
- Criteria for determining if the analysis was performed according to the QAPP and the SOW;
- Criteria and codes used to qualify data; and
- Criteria for summarizing and reporting the results of verification.

907 A discussion of verification can be found in Chapter 8, *Radiochemical Data Verification and*
908 *Validation.*

909 Data validation should be performed by an organization independent of the group that generated
910 the data to provide an unbiased evaluation. Validation procedures and criteria should be
911 established prior to the data evaluation. Requirements for data validation include the following:

912 • An approved list of well-defined MQOs and the action level(s) relevant to the project DQOs;

913 • Criteria for assigning qualifiers based on the approved list of MQOs;

914 • Criteria for identifying situations when the data validator's best professional judgement can
915 be employed and when a strict protocol must be followed; and

916 • Criteria for summarizing and reporting the results of validation.

917 A discussion of verification can be found in Chapter 8, *Radiochemical Data Verification and*
918 *Validation.*

919 **D5.2 Data Validation and Usability (D2): Verification and Validation Methods**

920 D5.2.1 Data Verification

921 Data verification or compliance with the SOW is concerned with: complete, consistent,
922 compliant and comparable data. Since the data verification report documents whether laboratory
923 conditions and operations were compliant with the SOW, the report is often used to determine
924 payment for laboratory services. Chapter 5, *Obtaining Laboratory Services*, discusses the need to
925 prepare a SOW for all radioanalytical laboratory work regardless of whether the work is
926 contracted out or performed in-house.

927 This element of the QAPP should address the following issues to ensure that data verification
928 will focus on the correct issues:

929 • Identify the documents (e.g., other QAPP sections, SOW, contracts, standard methods) that
930 describe the deliverables and criteria that will be used to evaluate compliance;

- Identify the performance indicators that will be evaluated (e.g., yield, matrix spikes, replicates). See Chapter 18, *Laboratory Quality Control*, for a discussion of radiochemistry performance indicators;

- Identify the criteria that will be used to determine "in-control" and "not-in-control" conditions;

- Identify who will perform data verification;

- Describe the contents of the verification report (e.g., a summary of the verification process as applied; required project activities not performed or not on schedule or not according to required frequency; procedures that were performed but did not meet acceptance criteria; affected samples; exceptions); and

- Identify who will receive verification reports and the mechanism for its archival.

D5.2.2 Data Validation

Chapter 8, *Radiochemical Data Verification and Validation*, discusses radiochemical data validation in detail. MARLAP recommends that a data validation plan document be included as an appendix to the QAPP. The data validation report will serve as the major input to the process that evaluates the reliability of measurement data.

This element of the QAPP should address the following issues:

- Describe the deliverables, measurement performance criteria and acceptance criteria that will be used to evaluate data validity;

- Identify who will perform data validation;

- Describe the contents of the validation report (e.g., a summary of the validation process as applied; summary of exceptional circumstances; list of validated samples, summary of validated results); and

- Identify who will receive validation reports and the mechanism for its archival.

D5.3 Data Validation and Usability (D3): Reconciliation with Data Quality Objectives

This element of the QAPP describes how project data will be evaluated to determine its usability in decision-making. This evaluation is referred to as the "data quality assessment." DQA is the process that scientifically and statistically evaluates project-wide knowledge in terms of the project objectives to assess the usability of data. DQA should be ongoing and integrated into the project data collection activities. On project diagrams and data life cycles, it is often shown as the last phase of the data collection activity. However, like any assessment process, DQA should be considered throughout the data collection activity to ensure usable data. EPA guidance (EPA, 1996) provides a detailed discussion of that part of the DQA process that addresses statistical manipulation of the data. In addition to statistical considerations, the DQA process integrates and considers information from the validation report, assessment reports, the field, the conceptual model and historical data to arrive at its conclusions regarding data usability. DQA is discussed in Chapter 9, *Data Quality Assessment.*

The DQA considers the impact of a myriad of data collection activities in addition to measurement activities. This element of the QAPP should direct those performing the DQA to:

- Review the QAPP and DQOs;
- Review the validation report;
- Review reports to management;
- Review identified field, sampling, sample handling, analytical and data management problems associated with project activities;
- Review all corrective actions; and
- Review all assessment reports and findings (e.g., surveillances, audits, performance evaluations, peer reviews, management and technical system reviews).

In addition to the above, this element of the QAPP should address the following issues:

- Identify who will perform the DQA;
- Identify what issues will be addressed by the DQA;
- Identify any statistical tests that will be used to evaluate the data (e.g., tests for normality);
- Describe how MQOs will be used to determine the usability of measurement data (i.e., did the measurement uncertainty in the data significantly affect confidence in the decision?);
- Describe how the representativeness of the data will be evaluated (e.g., review the sampling strategy, the suitability of sampling devices, subsampling procedures, assessment findings);
- Describe how the potential impact of non-measurable factors will be considered;
- Identify what will be included in the DQA report; and

- Identify who will receive the report and the mechanism for its archival.

D6.0 References

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APPENDIX E: CONTRACTING LABORATORY SERVICES

E.1 Introduction

This appendix provides general guidance on Federal contracting and contracting terminology as used for negotiated procurements. Federal Agencies, and laboratories doing business with them, must follow applicable provisions of the *Federal Acquisition Regulations* (FAR) and Agency-specific supplements. The examples provided in this appendix are based primarily on procedures followed by the U.S. Geological Survey (USGS).

This appendix addresses selecting a laboratory to establish services that supplement an Agency's in-house activities through the contracting of additional outside support. This appendix offers a number of principles that may be used when selecting a service provider, establishing a contractual agreement, and later working with a contract laboratory. These principles may also be applied to contractors that are located outside of the United States. In such cases, legal counsel will need to review and advise an Agency concerning pertinent issues related to international contracts.

This appendix also covers laboratory audits that are part of a final selection process and other activities that take place until the contract is concluded. Chapter 5 supports this appendix with a general description on how to obtain laboratory services. Chapter 7 complements this appendix by considering information related to laboratory evaluations that are conducted throughout the term of a project—whether or not this work is specifically covered by a contract.

Obtaining support for laboratory analyses is already a practice that is familiar to a number of Federal and State Agencies. The following discussion will apply:

- *Agency* - a Federal or State government office or department, (or potentially any other public or private institution) that offers a solicitation or other mechanism to obtain outside services;
- *Proposer* - a contracting firm or commercial facility that submits a proposal related to providing services; and
- *Contractor* - a firm that is awarded the contract and is engaged in providing analytical services.

Furthermore, the size and complexity of some agency projects will clearly exceed the extent of the information presented here. In its present form, this appendix serves to touch on many of the issues and considerations that are common to all projects, be they large or small.

MARLAP draws attention to another dimension of the overall contracting process by considering how the Data Quality Objectives (DQOs) and Measurement Quality Objectives (MQOs) are incorporated into every stage of a project—as described earlier in greater detail (Chapters 2 and 3). In this regard, an Agency's Project Managers and staff are given an opportunity to consider options with some foresight and to examine the larger picture, which concerns planning short- or long-term projects that utilize a contractor's services. As services are acquired, and later as work is performed, the specific concepts and goals outlined by the DQOs and MQOs will be revisited. This becomes an iterative process that offers the possibility to further define objectives as work is conducted. Whenever the DQOs or MQOs are changed, the contract should be modified to reflect the new specifications. Employing the MQOs and tracking the contractor's progress provides a means by which Project Managers and contract-laboratory technical staff can return and review the project at any point during the contract period. This allows for repeated evaluations to further optimize a project's goals and, if anticipated in the contract's language, perhaps even provides for the option to revise or redirect the way performance-based work is conducted.

The Office of Federal Procurement Policy (OFPP, 1997) has developed a Performance-Based Service Contracting review checklist to be used as a guide in developing a performance-based solicitation. The checklist contains minimum required elements that should be present for a contract to be considered performance-based. Performance-Based Service Contracting focuses on three elements: a performance work statement; a quality assurance project plan (QAPP); and appropriate incentives, if applicable. The performance work statement defines the requirements in terms of the objective and measurable outputs. The performance work statement should answer five basic questions: what, when, where, how many, and how well. The work statement should structure and clearly define the requirements, performance standards, acceptable quality levels, methods of surveillance, incentives if applicable and evaluation criteria. A market survey should be conducted so that the marketplace and other stakeholders are provided the opportunity to comment on draft performance requirements and standards, the proposed QA project plan, and performance incentives, if applicable.

A number of benefits arise from establishing a formal working relationship between an Agency and a contractor. For example:

- A contract is a legal document that clearly defines activities and expectations for the benefit of both parties engaged in the contractual relationship.

- The process of drafting language to cover legal considerations may well include contributions from legal staff. Legal guidance may be obtained as needed at any time during the planning stages or later when a contract is in place. However, the core of a contractor's proposal, and eventually the contract itself, provide the foundation of technical work that is required to complete a project or attain an ongoing program goal. *In this regard, aside from legal issues that are an integral part of every contract, this appendix's principal focus is on the laboratory process or technical work-related content of the contract.*

- The statement of work (SOW) first appears as part of the Agency's request for proposal (RFP) and later is essentially incorporated into the proposal by the proposer when responding to the RFP. When work is underway, the SOW becomes a working document that both the Agency and contractor refer to during the life of the contract.

- Legal challenges concerning project results (i.e., laboratory data) may arise during the contract period. The language in a contract should offer sufficient detail to provide the means to circumvent potential or anticipated problems. For example, attention to deliveries of samples to the laboratory on weekends and holidays or data reporting requirements that are designed to support the proper presentation of data in a legal proceeding are important aspects of many Federal- and State-funded contracts.

Overall, this appendix incorporates a sequence that includes both a planning and a selection process. Figure E-1 illustrates a series of general steps from planning before a contract is even in place to the ultimate termination of the contract. An Agency first determines a need as part of planning, and along the way advertises this need to solicit proposals from outside service providers who operate analytical laboratory facilities. Planning future work, advertising for, and later selecting services from proposals submitted to an Agency takes time—perhaps six or more months pass before a laboratory is selected, a contract is in place, and analytical work begins. The total working duration of a contract, for example, might cover services for a brief time (weeks or months) and in other cases, many contracts may run for a preset one-year period or for a more extended period of three to five years with optional renewal periods during that time.

The MARLAP user will find that planning employs a thought process much like that used to prepare an RFP. In general, one starts with questions that define a project's needs. Further, by developing Analytical Protocol Specifications (APSs) which include specific MQOs, one enters an iterative process such that—at various times—data quality is checked in relation to work

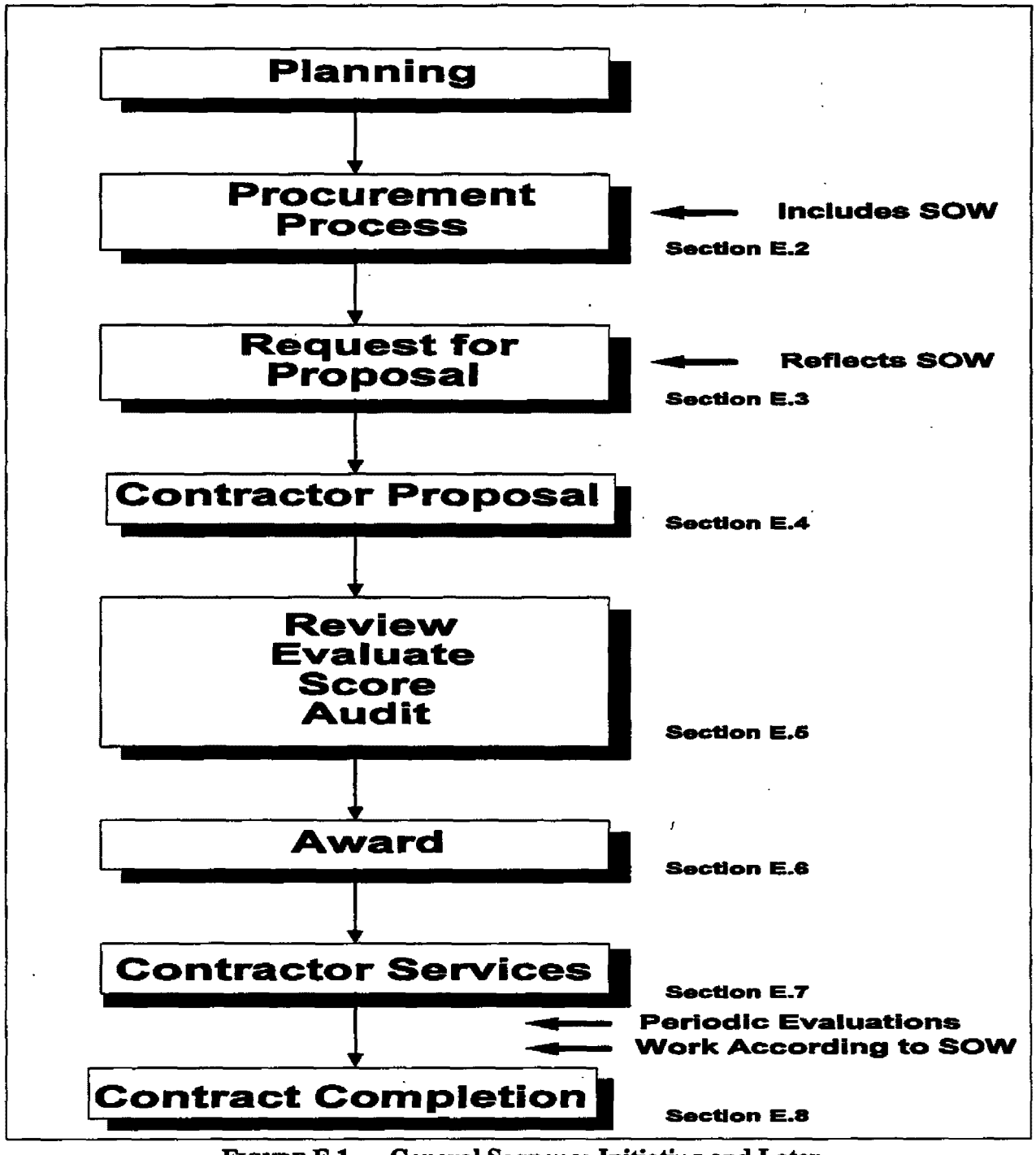

FIGURE E.1 — General Sequence Initiating and Later Conducting Work with a Contract Laboratory

performed both in-house and by the outside service provider. Overall, planning results in the development of a project plan document (e.g., QAPP). During planning, a Project Manager and the Agency staff can consider both routine and special analytical services that may be required to provide data of definable quality. The SOW serves to integrate all technical and quality aspects of the project, and to define how specific quality-assurance and quality-control activities are implemented during the time course of a contract. Also, at an early stage in planning, the Agency may choose to assemble a team to serve as the Technical Evaluation Committee (TEC; Section E.5.1). The main role of the TEC is in selecting the contract laboratory by reviewing proposals and by auditing laboratory facilities. The TEC is discussed later in this appendix, however, the key issue here concerns the benefit to establishing this committee early on, even to the point of including TEC members in the initial planning activities. The result is a better informed evaluation committee and a team of individuals that can help make adjustments when the directed planning process warrants an iterative evaluation of the way work is performed under the contract. Overall, planning initiates the process that characterizes the nature of the contracting process to follow.

E.2 Procurement of Services

Recognizing that the procurement process differs from Agency to Agency, the following guidance provides a general overview to highlight considerations that may already be part of—or be incorporated into—the current practice. First, the request for specific analytical services can be viewed as a key product of both the Agency's mission and the directed planning process. As Agency staff ask questions, list key considerations to address during the work, and in turn define objectives, they also eliminate unnecessary options to help focus on the most suitable contracting options that satisfy the APSs. Thereafter, the scope of the work, schedule, manpower constraints, availability of in-house engineering resources, and other technical considerations all enter into estimating and defining a need for project support. This approach refines the objectives and establishes needs that may be advertised in a solicitation for outside services. The resulting work or project plan should clearly articulate what is typically known but not limited to the following:

- Site conditions;
- Analytes of interest;
- Matrices of concern;
- How samples are to be collected and handled;
- Custody requirements;
- Data needs and APSs, including the MQOs;
- Stipulated analytical methods, if required
- Applicable regulations; and

- Data reporting.

All of this defines the scope of work, such that the Agency can initiate a formal request for proposals or arrange for an analysis request as part of a less formal procurement.

E.2.1 Request for Approval of Proposed Procurement Action

If required within an Agency, a request is processed using forms and related paperwork to document information typically including, but not limited to, the following:

- Identification of product or service to be procured;
- Title of program or project;
- Description of product or service;
- Relationship of product or service to overall program or project;
- Funding year, projected contract life, amounts, etc.;
- Name and phone number of Project Officer(s);
- Signature of Project Officer and date
- Name and phone number of Contracting Officer; and
- Signature of Contracting Officer and date.

An Agency may also be required to collect or track information for an RFP with regard to:

- New procurements: type of contract, grant, agreement, proposal, etc. Continuing procurements: pre-negotiated options, modifications, justification for non-competitive procurement, etc.
- Source information: small business or other set aside, minority business, women-owned business, etc.

In addition to the information listed above, Agency-specific forms used to initiate a procurement request may also provide a place to indicate Agency approval with names, signature lines, and date spaces for completion by officials in the office responsible for procurement and contracts. An Agency administrator or director above the level of the office of procurement may also sign this form indicating Agency approval.

E.2.2 Types of Procurement Mechanisms

Table E.1 lists many of the procurement options available to the Project Manager. Each option offers a solution to a specific need. For example, a purchase order is typically appropriate for

tasks with a somewhat limited scope and thus is perhaps most useful when samples are to be processed on a one-time basis. In some cases where only one or a limited number of vendors can fulfill the needs of the project, e.g., low-level tritium analysis by helium ingrowth within a specified time period, a sole source solicitation is commonly used.

TABLE E.1— Examples of Procurement Options to Obtain Materials or Services.

Procurement Mechanism	Example of Specific Use or Application
Purchase order	In-house process handled through purchasing staff; limited to small needs without a formal request or used in conjunction with a solicitation (competitive process) and a limited amount of funding; commonly used to purchase equipment and supplies, but may be used for processing samples.
Sole source solicitation	In specific instances, a single or a limited number of service providers are able to offer specific services.
Request for Quotation (RFQ)	Formal, main process for establishing contracts—generally addresses a major, long-term need for contractor support; this is a competitive process based mainly on cost.
Request for Proposal (RFP)	Formal, main process for establishing contracts—generally addresses a major, long-term need for contractor support; this is a competitive process based mainly on technical capability.
Modification to an existing contract or delivery order	This approach meets a need that is consistent with the type of contract that is in place, e.g., Agency amends contract to add a method for sample processing that is similar to work already covered.
Basic Ordering Agreement (BOA)	Work is arranged with a pre-approved laboratory as described in Section E.2.2.

The process leading to a formal contract provides a more comprehensive view of nearly every aspect of the work that an Agency expects from a contractor. The formal process includes three types of procurement: Request for Quotation (RFQ), Request for Proposal (RFP), and the Basic Ordering Agreement (BOA). The RFQ solicits bidders to provide a quotation for laboratory services that have been detailed in the solicitation. The specifications may include the technical, administrative, and contractual requirements for a project. For the RFQ, the contract typically is awarded to the lowest bidder that can fulfill the contract specifications without regard to the quality of the service. What appears to be a good price may not entail the use of the best or most appropriate method or technology. There may be significant advantages in seeking to acquire high-technology services as a primary focus in advance of, or along with, concerns pertaining to price.

For an RFP, there is considerably more work for the Agency and the laboratory. The laboratory must submit a formal proposal addressing all key elements of the solicitation that include how,

why, what, when ,where and by whom the services are to be performed. The TEC or Contracting Officer must review all proposals, rank them according to a scoring system and finally assess the cost effectiveness of the proposals before making the final award.

The BOA provides a process that serves to pre-approved service providers. This includes a preliminary advertisement for a particular type of work, such as radioanalytical services. The Agency then selects and approves a number of candidates that respond to the advertisement. With this approach, the Agency assembles a potential list of approved laboratories that are contacted as needed to support specific needs. The Agency may choose to simply write a task order (defining a specific scope of work) with a specific pre-approved laboratory, or the Agency may initiate a competitive bidding process for the task order between several or all members on the list of pre-approved laboratories. Once chosen, the laboratory may be guided by a combined Statement of Work or Task Order that is issued by the Agency.

Mechanisms that permit an Agency to obtain analyses for a limited number of samples—without an established contractual relationship with a specific contractor—may simply be necessitated by the small number of samples, time constraints where specific analyses are not part of an existing contract, limitations related to funding, or other consideration. The formal business and legal requirements of a long-term relationship warrant a stronger contractual foundation for work conducted in a timely fashion, on larger numbers of samples, and over specified periods of time. The contracts described above, with the exception of a BOA, are considered "requirement" contracts and requires the group initiating the solicitation to use only the contracted laboratory, without exception, for the contract period to perform the sample analyses.

E.3 Request for Proposals—The Solicitation

To appreciate the full extent of a competitive process leading to a formal working relationship—between an Agency and a contractor—*the primary example used hereafter is the solicitation and selection process that starts with the issuance of a* RFP, as shown in Figure E-1.

Federal announcements of certain RFPs can be found in the *Commerce Business Daily* (CBD). The CBD primarily provides a synopsis or brief description of the type of work the Agency is interested in purchasing. States and local governments also solicit proposals and announce the availability of work in USABID (a compilation of solicitations from hundreds of city, county, and state agencies). Internet sites that offer access to the CBD (http://cbdnet.access.gpo.gov/) and USABID listings can be located through electronic searches using Web Browser software. Once a site is located, the information can be viewed through public access or commercial Internet-based services. In other cases, a State or Federal Agency may maintain a mailing list with names

and addresses for potentially interested parties. This might include contractors that previously supported the Agency or others who have volunteered information for the mailing list.

Once the RFP, State advertisement, or other form of solicitation is publicized, interested parties can contact the appropriate Agency to obtain all the specific information relevant to completing a candidate laboratory's contract proposal. For the present discussion, this information is contained in the text of the RFP document. The RFP may be accompanied by a cover letter stating an invitation to applicants and general information related to the content of a proposal and specific indication for the types of sections or sub-sections the proposal will contain. For example, a proposal divided into three sections technical proposal, representations and certifications, and price proposal allows the Agency to separate pricing from technical information. In this way, the Agency considers each candidate first on technical merits before the price of services enters the selection process.

The Agency's RFP is designed to provide a complete description of the proposed work. For example, a RFP should inform all candidate laboratories (i.e., proposers) of the estimated number of samples that are anticipated for processing under the contract. The description of work in the RFP as described in the SOW serves to indicate the types of radionuclide analyses required for the stated sample types and the number of samples to undergo similar or different processing protocols. The estimate also has a bearing on cost and other specific project details as described in the SOW. Additional information provided with the RFP serves to instruct the proposer regarding other technical requirements (APSs), the required number of copies of each section of the proposal, proposal deadline, address where proposals are to be sent, and other general concerns or specifications relevant to the solicitation.

The cover letter may indicate how each proposer will be notified if its proposal is dropped from the competitive range of candidates during the selection process. The letter may also include precautionary notes concerning whom to contact or not contact at the Agency regarding the potential contract during the competitive process. Finally, if particular sources are encouraged to apply (e.g., minority or small business), this information will be mentioned in the Agency's invitation to apply.

E.3.1 Market Research

The Office of Federal Procurement Policy (OFPP, 1997) recommends that the marketplace and other stakeholders be provided the opportunity to comment on draft performance requirements and standards. This practice allows for feedback from those people working in the technical

community so that their comments may be incorporated into the final RFP and the potential offerors can develop intelligent proposals.

E.3.2 Length of Contract

The time and resources involved in writing and awarding a major contract generally make it impractical and cost ineffective to award contracts for less than one or more years. While contracts running for shorter terms are sometimes established, single or multiple year terms are commonly used to provide the necessary services for some Federal or State programs. Monitoring programs are likely to go long periods of time with renewals or RFPs that continue the work into the future. Elsewhere, relatively large projects conducting radiation survey and site investigations may require a contract process that, for the most part, estimates the time services will be needed to finish work through to the completion of a final status survey. In this case, the contract may specify any length of time, but also include the option to renew the contract for a period of time to bring the project to a close. The relationship between the length of a contract and the type of project can be part of the structured planning process that seeks to anticipate every facet of a project from start to finish.

Multi-year contracts are typically initiated with an award for the first year followed by an additional number of one-year options. In this way, a five-year contract is awarded for 1 year with four one-year option periods to complete the contract's full term. Problems that arise during any year may result in an Agency review of the MQOs or an examination of the current working relationship that may result in the Agency's decision to not extend the contract into the next option year.

E.3.3 Subcontracts

For continuity or for quality assurance (QA), the contract may require one laboratory to handle the entire analytical work load. However, subcontracting work with the support of an additional laboratory facility may arise if the project plan calls for a large number of samples requiring quick turnaround times and specific methodologies that are not part of the primary laboratory's support services. A proposer may choose to list a number of subcontractors in the proposal. The listing may or may not include other laboratories with whom the proposer has an existing or prior working relationship. The choice of subcontracting firms may be limited during the proposal process. There may be many qualified service providers to meet specific project needs. However, once work is under way, using a limited number of laboratories that qualify for this secondary role helps maintain greater control of quality and thus the consistency of data coming from more

than a single laboratory alone. Furthermore, the contractor may prefer working with a specific subcontractor, but this arrangement is subject to Agency approval.

The use of multiple service providers adds complexity to the Agency's tasks of auditing, evaluating, and tracking services. The contractor and their subcontractor(s) are held to the same terms and conditions of the contract. The prime contractor is held responsible for the performance of its subcontract laboratories. In some instances, certain legal considerations related to chain of custody, data quality and reporting, or other concern may limit an Agency's options and thus restrict the number of laboratories that are part of any one contract.

E.4 Proposal Requirements

The Agency's RFP will state requirements that each proposer is to cover in its proposal. The proposal document itself becomes first the object of evaluation and is a reflection of how the contract and the SOW are structured. Whether one works with a formal contract or a simpler analysis request, the Agency and contractor need to agree to all factors concerning the specific analytical work. Where written agreements are established, the language should be specific to avoid disputes. Clear communication and complete documentation are critical to a project's success. For example, the Agency's staff asks questions of itself during the planning process to create and later advertise a clearly stated need in the RFP. The contractor then composes a proposal that documents relevant details concerning their laboratory's administrative and technical personnel, training programs, instrumentation, previous project experience, etc. Overall, the proposer should make an effort to address every element presented in the RFP. The proposer should be as clear and complete as possible to ensure a fair and proper evaluation during the Agency's selection process.

The planning process will reveal numerous factors related to technical requirements necessary to tailor a contract to specific project needs. The following sections may be reviewed by Agency staff (radiochemist or TEC) during planning to determine if additional needs are required beyond those listed in this manual. Agency personnel should consider carefully the need to include every necessary detail to make a concise RFP. The proposer can read the same sections to anticipate the types of issues that are likely to appear in an RFP and that may be addressed in a proposal.

E.4.1 RFP and Contract Information

There are two basic areas an Agency can consider when assembling information to include in an RFP. The proposer is expected to respond with information for each area in its proposal. The first area includes a listing of *General Laboratory Requirements and Activities*. The second area,

Technical Components to Laboratory Functions, complements the first, but typically includes more detailed information.

1) General Laboratory Requirements
- Personnel;
- Facilities;
- Meeting Contract Data Quality Requirements;
- Schedule;
- Quality Manual;
- Data Deliverables Including Electronic Format;
- Licenses and Certifications; and
- Experience: Previous and Current Contracts; Quality of Performance.

2) Technical Components to Laboratory Functions
- Standard Operating Procedures;
- Instrumentation
- Training
- Performance Evaluation Programs; and
- Quality System.

The laboratory requirements and technical components indicated above are addressed in this appendix. Beyond this, there are additional elements that may be required to appear with detailed descriptions in an RFP and later in a formal proposal. One significant portion of the RFP, and a key element appearing later in the contract itself, is the SOW. This is the third area a proposer is to address, and information in a SOW may vary depending on the nature of the work.

The Agency will provide specifications in the RFP regarding the work the contractor will perform. This initiates an interaction between a proposer and the Agency and further leads to two distinct areas of contractor-Agency activity. The first concerns development and submitting of proposals stating how the laboratory work will be conducted to meet specific Agency needs. The second concerns Agency evaluations of the laboratory's work according to contract specifications (Section E.5) and the SOW. Once the contract is awarded, a contractor is bound to perform the work as proposed.

Specific sections of each contract cover exactly what is expected of the contractor and its analytical facilities to fulfill the terms and conditions of the contract. The SOW describes the required tasks and deliverables, and presents technical details regarding how tasks are to be executed. A well written SOW provides technical information and guidance that directs the

contractor to a practice that is technically qualified, meets all relevant regulatory requirements, and appropriately coordinates all work activities. A sample checklist for key information that may be in a SOW is presented in Table E.2. Note that not all topics in the list are appropriate for each project, and in some cases, only a subset is required. The list may also be considered in relation to less formal working relationships (e.g., purchase order), as well as tasks covered in formal contracts.

TABLE E.2 — SOW Checklists for the Agency and Proposer

SAMPLE HISTORY
- ____ General background on the problem
- ____ Site conditions
- ____ Regulatory background
- ____ Sample origin
- ____ Analytes and interferences (chemical forms and estimated concentration range)
- ____ Safety issues
- ____ Data use
  - ____ Regulatory compliance
  - ____ Litigation

ANALYSIS RELATED
- ____ Number of samples
- ____ Matrix
- ____ Container type and volume
- ____ Receiving and storage requirements
- ____ Special handling considerations
- ____ Custody requirements
- ____ Preservation requirements, if any
- ____ Analytes of interest (specific isotopes or nuclide)
- ____ Measurement Quality Objectives
- ____ Proposed method (if appropriate) and method validation documentation
- ____ Regulatory reporting time requirement (if applicable)
- ____ Analysis time requirements (time issues related to half-lives)
- ____ QC requirements (frequency, type, and acceptance criteria)
- ____ Waste disposal issues during processing
- ____ Licenses and accreditation

OVERSIGHT
- ____ Quality manual
- ____ Required Performance Evaluation Program participation
- ____ Criteria for (blind) QC
- ____ Site visit/data assessment
- ____ Audit (if any)

REPORTING REQUIREMENTS
- ____ Report results as gross, isotopic....
- ____ Reporting units
- ____ Reporting basis (dry weight, ...)
- ____ How to report measurement uncertainties

___ Reporting Minimum Detectable Concentration and Minimum Quantifiable Concentration
___ Report contents desired and information for electronic data transfer
___ Turn-around time requirements
___ Electronic deliverables
___ Data report format and outline

NOTIFICATION
___ Exceeding predetermined Maximum Concentration Levels - when applicable
___ Batch QC failures or other issues
___ Failure to meet analysis or turnaround times
___ Violations related to radioactive material license
___ Change of primary staff associated with contract work

SCHEDULE
___ Expected date of delivery
___ Method of delivery of samples
___ Determine schedule (on batch basis)
___ Method to report and resolve anomalies and nonconformance in data to the client
___ Return of samples and disposition of waste

CONTACT
___ Name, address, phone number of responsible parties

E.4.2 Personnel

The education, working knowledge, and experience of the individuals that supervise operations, conduct analyses, operate laboratory instruments, process data, and create the deliverables is of key importance to the operation of a laboratory. The Agency is essentially asking: *Who is sufficiently qualified to meet the proposed project's needs?* (The answer to this question may come from an Agency's guidance or other specific requirements generated by the structured planning process.) The laboratory staff that will perform the analyses should be employed, trained, and qualified prior to the award of the contract.

In response to the RFP, the proposer should include a listing of staff members capable of managing, receiving, logging, preparing, and processing samples; providing reports in the format specified by the project; preparing data packages with documentation to support the results; maintaining the chain of custody; and other key work activities. The laboratory should list the administrative personnel and appoint a technical person to be a point of contact for the proposed work. This person should fully understand the project's requirements and be reasonably available to respond to every project need. A proposal should include the educational background and a brief resume for all key personnel. The level of training for each technician should be included.

Tables E.3 and E.4 are examples that briefly summarize the suggested minimum experience, education, and training for the listed positions. Note, some Agency-specific requirements may exceed the suggested qualifications and this issue should be explored further during the planning process. The goal here is to provide basic guidance with examples that the MARLAP user can employ as a starting point during planning. Once specific requirements are established, this information will appear in the RFP.

Table E.3 provides a listing for the types of laboratory technical supervisory personnel that are likely to manage every aspect of a laboratory's work. Each position title is given a brief description of responsibilities, along with the minimum level of education and experience. Table E.4 presents descriptions for staff members that may be considered optional personnel or, in some cases, represent necessary support that is provided by personnel with other position titles. Table E.5 indicates the minimum education and experience for laboratory technical staff members. In some cases, specific training may add to or be substituted for the listed education or experience requirement. Training may come in a number of forms, such as instrument-specific classes offered by a manufacturer, to operational or safety programs given by outside trainers or the laboratory's own staff.

TABLE E.3 — Laboratory Technical Supervisory Personnel Listed by Position Title and Examples for Suggested Minimum Qualifications.

All personnel are responsible to perform their work to meet all terms and conditions of the contract.

Technical Supervisory Personnel		
Position Title and Responsibilities	**Education**	**Experience**
Radiochemical Laboratory Supervisor, Director, or Manager. Responsible for all technical efforts of the radiochemical laboratory.	Minimum of Bachelor's degree in any scientific/engineering discipline, with training in radiochemistry, radiation detection instrumentation, statistics, and QA.	Minimum of three years of radioanalytical laboratory experience, including at least one year in a supervisory position. Training in laboratory safety, including radiation safety.
Quality Assurance Officer Responsible for overseeing the quality assurance aspects of the data and reporting directly to upper management.	Minimum of Bachelor's degree in any scientific/engineering discipline, with training in physics, chemistry, and statistics.	Minimum of three years of laboratory experience, including at least one year of applied experience with QA principles and practices in an analytical laboratory or commensurate training in QA principles.

TABLE E.4 — Laboratory Technical Personnel Listed by Position Title and Examples for Suggested Minimum Qualifications and Examples of Optional Staff Members

Optional Technical Personnel		
Position Title and Responsibilities	**Education**	**Experience**
Systems Manager Responsible for the management and quality control of all computing systems; generating, updating, and quality control for deliverables.	Minimum of Bachelor's degree with intermediate courses in programming, information management, database management systems, or systems requirements analysis.	Minimum of three years experience in data or systems management of programming, including one year experience with the software being utilized for data management and generation of deliverables.
Programmer Analyst Responsible for the installation, operation, and maintenance of software and programs, generating, updating, and quality of controlling analytical databases and automated deliverables.	Minimum of Bachelor's degree with intermediate courses in programming, information management, information systems, or systems requirements analysis.	Minimum of two years experience in systems or applications programming, including one year experience with the software being utilized for data management and generation of deliverables.

TABLE E.5 — Laboratory Technical Staff Listed by Position Title and Examples for Suggested Minimum Qualifications

All personnel are responsible to perform their work to meet all terms and conditions of the contract.

Technical Staff		
Position Title	**Education**	**Experience**
Gamma Spectrometrist	• Minimum of Bachelor's degree in chemistry or any physical scientific/engineering discipline. • Training courses in gamma spectrometry.	• Minimum two years experience in spectrometric data interpretation. • Formal training or one year experience with spectral analysis software used to analyze data.
Alpha Spectrometrist	Minimum of Bachelor's degree in chemistry or any physical scientific/engineering discipline. • Training courses in alpha spectrometry.	Formal training or one year experience with spectral analysis software used to analyze data.

Position Title	Education	Experience
Radiochemist	Minimum of Bachelor's degree in chemistry or any physical scientific/engineering discipline. In lieu of the educational requirement, two years of additional, equivalent radioanalytical experience may be substituted.	Minimum of two years experience with chemistry laboratory procedures, with at least one year of radiochemistry in conjunction with the educational qualifications, including (for example): 1) Operation and maintenance of radioactivity counting equipment; 2) Alpha/gamma spectrometric data interpretation; 3) Radiochemistry analytical procedures; and 4) Sample preparation for radioactivity analysis.
Counting Room Technician	Minimum of Bachelor's degree in chemistry or any scientific/engineering discipline.	Minimum of one year experience in a radioanalytical laboratory.
Laboratory Technician	Minimum of high school diploma and a college level course in general chemistry or equivalent—or college degree in another scientific discipline (e.g., biology, geology, etc.)	Minimum of one year experience in a radioanalytical laboratory.

E.4.3 Instrumentation

A proposer's laboratory must have in place and in good working order the types and required number of instruments necessary to perform the work advertised by the Agency. Specific factors are noted in the RFP, such as: an estimate for the number of samples, length of the contract, and expected turnaround times which influence the types of equipment needed to support the contract.

Analytical work can be viewed as a function of current technology. Changes may occur from time to time, especially in relation to scientific advancements in equipment, software, etc. Instrumentation represents the mechanical interface between prepared samples and the data generated in the laboratory. The capacity to process larger and larger numbers of samples while sustaining the desired level of analytical sensitivity and accuracy is ultimately a function of the laboratory's equipment, and the knowledge and experience of the individuals who operate and maintain the instruments. Additional support for the laboratory's on-line activities or the state of readiness to maintain a constant or an elevated peak work load comes in the form of back-up instruments that are available at all times. Information concerning service contracts that provide repairs or replacement when equipment fails to perform is important to meeting contract obligations. Demonstrating that this support will be in place for the duration of the contract is a key element for the proposer to clearly describe in a proposal.

E.4.3.1 Type, Number, and Age of Laboratory Instruments

A description of the types of instruments at a laboratory is an important component of the proposal. The number of each type of instrument available for the proposed work should be indicated in the proposal. This includes various counters, detectors, or other systems used for radioanalytical work. A complete description for each instrument might include the age or acquisition date. This information may be accompanied by a brief description indicating the level of service an instrument provides at its present location.

E.4.3.2 Service Contract

The types and numbers of service contracts may vary depending on the service provider. Newly purchased instruments will be covered by a manufacturer's warranty. Other equipment used beyond the initial warranty period may either be supported by extensions to the manufacturer's warranties or by other commercial services that cover individual instrument or many instruments under a site-wide service contract. Whatever type of support is in place, the contractor will need to state how having or not having such service contracts affects the laboratory's ability to meet the terms of the contract and the potential impact related to the SOW.

E.4.4 Narrative to Approach

A proposal can "speak" to the Agency's evaluation team by providing a logical and clearly written narrative of how the proposer will attend to every detail listed in the RFP. This approach conveys key information in a readable format to relate a proposer's understanding, experience, and working knowledge of the anticipated work. In this way, the text also illustrates how various components of the proposal work together to contribute to a unified view of the laboratory functions given the proposed work load as described in the RFP and as detailed in the SOW. The next four sections provide examples of proposal topics for which the proposer may apply a narrative format to address how the laboratory is qualified to do the proposed work.

E.4.4.1 Analytical Methods or Protocols

The proposer should list all proposed methods they plan to use. The proposal should also furnish all required method validation documentation to gain approval for use. When addressing use of methods, the proposer can describe how a method exhibits the best performance and also offer specific solutions to meet the Agency's needs.

E.4.4.2 Meeting Contract Measurement Quality Objectives

The Agency's planning process started with a review of questions and issues concerned with generating specific project APSs/MQOs. Stating how a proposer intends to meet the APSs/MQOs data quality requirements adds an important section to the proposal. This allows the competing laboratories to demonstrate that they understand the requirements of the contract and their individual approaches to fulfilling these requirements. Further evidence in support of the proposer's preparations to meet or exceed the Agency's data quality needs is generally covered in a contract laboratory's Quality Manual (Section E.4.5).

E.4.4.3 Data Package

The proposer responds to the RFP by stating how data will be processed under the contract. A narrative describing the use of personnel, equipment, and facilities illustrates every step in obtaining, recording, storing, formatting, documenting and reporting sample information and analytical results. The specific information related to all these activities and the required information as specified by the SOW is gathered into a data package. For example, a standard data package includes a case narrative, the results (in the format specified by the Agency), a contractor data review checklist, any non-conformance memos resulting from the work, Agency and contractor-internal chains of custody, sample and quality control (QC) sample data (this includes a results listing, calculation file, data file list, and the counting data) and continuing calibration data, and standard and tracer source-trace information, when applicable. At the inception of a project, initial calibration data are provided for detectors used for the work. If a detector is re-calibrated, or a new detector is placed in service, initial calibration data are provided whenever those changes apply to the analyses in question.

Specific data from the data package may be further formatted in reports, including electronic formats, as the required deliverables which the contractor will send to the Agency. The delivery of this information is also specified according to a set schedule.

E.4.4.4 Schedule

The RFP will provide information that allows the proposer to design a schedule that is tailored to the Agency's need. For example, samples that are part of routine monitoring will arrive at the laboratory and the appropriate schedule reflects a cycle of activity from sample preparation to delivering a data package to the Agency. This type of schedule is repeatedly applied to each set of samples. Other projects, surveys, or studies may follow a time line of events from start to completion, with distinct sets of samples and unique needs that arise at specific points in time.

The proposer will initially outline a schedule that may utilize some cycling of activities at various stages of the work, but overall the nature of the work may change from stage to stage. The schedule in this case will reflect how the contractor expects to meet certain unique milestones on specific calendar dates.

Some projects will have certain requirements to process samples according to a graded processing schedule. The SOW should provide the requirements for the radiological holding time and sample processing turnaround time. Radiological holding time refers to the time required to process the sample—the time differential from the sample receipt date to the final sample matrix counting date. The sample processing turnaround time normally means the time differential from the receipt of the sample at the laboratory (receipt date) to the reporting of the analytical results to the Agency (analytical report date). As such, the turnaround time includes the radiological holding time, the time to generate the analytical results, and the time to report the results to the Agency.

Typically, three general time-related categories are stated: routine, expedited, and rush. Routine processing is normally a 30-day turnaround time, whereas expedited processing may have a turnaround time greater than five days but less than 30 days. Rush sample processing may have a radiological holding time of less than five days. For short-lived nuclides, the RFP should state the required radiological holding time, wherein the quantification of the analyte in the sample must be complete within a certain time period. The reporting of such results may be the standard 30-day turnaround time requirement. The Agency should be reasonable and technically correct in developing the required radiological holding and turnaround times.

The RFP should specify a schedule of liquidated or compensatory damages that should be imposed when the laboratory is non-compliant relative to technical requirements, radiological holding times, or turnaround times.

E.4.4.5 Sample Storage and Disposal

The RFP should specify the length of time the contractor must store samples after results are reported. In addition, it should state who is economically and physically responsible for the disposal of the samples. The laboratory should describe how the samples will be stored for the specified length of time and how it plans to dispose of the samples in accordance with local, State and Federal regulations.

E.4.5 Quality Manual

Only those radiochemistry laboratories that adhere to well-defined quality assurance procedures —pertaining to data validation, internal and external laboratory analytical checks, instrument precision and accuracy, personnel training, and setting routine laboratory guidelines—can insure the highest quality of scientifically valid and defensible data. In routine practice, a laboratory prepares a written description of its quality manual that addresses, at a minimum, the following items:

- Organization and Management
- Quality System Establishment, Audits, Essential Quality Controls and Evaluation and Data Verification;
- Personnel (Qualifications and Resumes);
- Physical Facilities - Accommodations and Environment;
- Equipment and Reference Materials;
- Measurement Traceability and Calibration;
- Test Methods and Standard Operating Procedures (Methods);
- Sample Handling, Sample Acceptance Policy and Sample Receipt;
- Records;
- Subcontracting Analytical Samples;
- Outside Support Services and Supplies; and
- Complaints.

The quality manual may be a separately prepared document that may incorporate or reference already available and approved laboratory standard operating procedures (SOPs). This manual provides sufficient detail to demonstrate that the contractor's measurements and data are appropriate to meet the MQOs and satisfy the terms and conditions of the contract. The manual should clearly state the objective of the SOP, how the SOP will be executed, and which performance standards will be used to evaluate the data. Work-related requirements based on quality assurance are also an integral part of the SOW.

When a proposal is submitted for review, the contracting laboratory generally sends along a current copy of its quality manual. Additional details pertaining to the content of a quality manual can be found in NELAC (2000), ASQC (1995), EPA (1993, 1994, 1997a), ISO/IEC (17025), and MARSSIM (2000).

E.4.6 Licenses and Accreditations

All laboratories must have appropriate licenses from the U.S. Nuclear Regulatory Commission (NRC) or other jurisdictions (Agreement State, host nation, etc.) to receive, possess, use, transfer, or dispose of radioactive materials (i.e., those licensable as indicated in 10 CFR 30.70, Schedule A—Exempt concentrations). A license number and current copy of a laboratory's licenses are typically requested with paperwork that one submits to obtain radionuclide materials—for example, when ordering and arranging to use laboratory standards. Overall, a laboratory's license permits work with certain radionuclides and limits to the quantity of each radionuclide at the laboratory. A proposer's license should allow for new work with the types and anticipated amounts of radionuclides as specified in an RFP. Part of the licensing requirement ensures that the laboratory maintains a functioning radiation safety program and properly trains its personnel in the use and disposal of radioactive materials. For more complete information on license requirements, refer to either the NRC, the appropriate State office, or 10 CFR 30.

The laboratory may need to be certified for radioassays by the State in which the lab resides. The RFP should request a copy of the current standing certification(s) to be submitted with the proposal. If the Agency expects a laboratory to process samples from numerous States across the United States, then additional certifications for other States may or will be required. To request that a proposer arrange for certification in multiple States prior to submitting a proposal may be viewed as placing an unfair burden on a candidate laboratory who as yet to learn if it will be awarded a contract. Additional fees, for each State certification, potentially add to a proposer's cost to simply present a proposal. In such cases, an Agency may indicate that additional certification(s)—above that already held for the laboratory's State of residence—may be required once the contract is awarded and just prior to initiating the work.

E.4.7 Experience

The contractor, viewed as a single entity made of all its staff members, may have an extensive work history as is exemplified through the number and types of projects and contracts that were previously or are currently supported by its laboratory services. This experience is potentially an important testimonial to the kind of work the contractor is presently able to handle with a high degree of competence. The Agency's evaluation team will review this information relative to the need(s) stated in the RFP. The more applicable the track record, the stronger a case the proposer has when competing for the award.

659 E.4.7.1 Previous or Current Contracts

660 In direct relation to the preceding section, the proposer's staff should respond directly to the RFP
661 when asked to provide a list of contracts previously awarded and those they are presently
662 fulfilling. Of primary importance, the list should contain contracts that are similar to the one
663 under consideration (i.e., similar work load and technical requirements), with the following
664 information:

665 • Name of the company or Agency awarding the contract;
666 • Address;
667 • Phone number;
668 • Name of contact person; and
669 • Scope of contract.

670 E.4.7.2 Quality of Performance

671 The Agency's TEC (Section E.5.1) is likely to check a laboratory's results for its participation in
672 a proficiency program which is sponsored by one of several Federal agencies. For example, the
673 U.S. Department of Energy (DOE), and National Institute of Standards and Technology (NIST)
674 offer proficiency programs. Records for the laboratory's results may be reviewed to cover a
675 number of years. This review indicates quality and consistency in relation to the types of samples
676 that the Federal Agency sends to each laboratory. Thus, at designated times during each year, a
677 laboratory will receive, process, and later report findings for proficiency program samples. This
678 routine is also required for certification by an Agency, such as the U.S. Environmental Protection
679 Agency (EPA) for drinking water analysis. In this case, to obtain or maintain a certification, the
680 laboratory must pass (i.e., successfully analyze) on the basis of a specific number of the total
681 samples.

682 E.5 Proposal Evaluation and Scoring Procedures

683 The initial stages of the evaluation process separate technical considerations from cost. Cost will
684 enter the selection process later on. The Agency's TEC will consider all proposals and then make
685 a first cut (Table E.6 and Section E.5.3 below), whereby some proposals are eliminated based on
686 the screening process. This selection from among the candidates is based on predetermined
687 criteria that are related to the original MQOs and how a proposer's laboratory is technically able
688 to support the contract. A lab that is obviously unequipped to perform work according to the
689 SOW is certain to be dropped early in the selection process. In some cases, the stated ability to
690 meet the analysis request should be verified by the Agency, through pre-award audits and

proficiency testing, as described below. Letters notifying unsuccessful bidders may be sent at this time. For information concerning a proposer's response to this letter, see Section E.5.7.

E.5.1 Evaluation Committee

The Agency personnel initially involved in establishing a new contract and starting the selection process include the Contract Officer (administrative, non-technical) and Contracting Officer's Representative (technical staff person). Once all proposals are accepted by the Agency, a team of technical staff members score the technical portion of the proposal. The team is lead by a chairperson who oversees the activities of this TEC. It is recommended that all members of the TEC have a technical background relevant to the subject matter of the contract.

One approach to evaluation includes sending copies of all proposals to each member of the committee for individual scoring (Table E.6). The Agency, after an appropriate length of time, may conduct a meeting or conference call to discuss the scores and reach a unified decision. Using this approach, each proposal is given a numerical score and these are listed in descending order. A "break-point" in the scores is chosen. All candidates above this point are accepted for a continuation of the selection process. Those below the break point may be notified at this point in time. Note that evaluations performed by some agencies may follow variations on this scoring and decision process.

The TEC must have a complete technical understanding of the subject matter related to the proposed work and the contract that is awarded at the end of the selection process. These individuals are also responsible for responding to any challenge to the Agency's decision to award the contract. Their answers to such challenges are based on technical merit in relation to the proposed work (Section E.5.7).

E.5.2 Ground Rules — Questions

The Agency's solicitation should clearly state if and when questions from an individual proposer will be allowed during the selection process. Information furnished in the Agency's response is simultaneously sent to all competing laboratories.

E.5.3 Scoring/Evaluating Scheme

The Agency should prepare an RFP that includes information concerning scoring of proposals or weights for areas of evaluation. This helps a proposer to understand the relative importance of specific sections in a proposal and how a proposal will be scored. In this case, the method of

evaluation and the scoring of specific topic areas is outlined in the solicitation. If this information is not listed in the solicitation and because evaluation formats differ Agency to Agency, proposers may wish to contact the Agency for additional Agency-specific details concerning this process.

An Agency may indicate the relative weight an evaluation area holds with regard to the proposed work for two principle reasons. First, the request is focused to meet a need for a specific type of work for a given study, project, or program. This initially allows a proposer to concentrate on areas of greatest importance. Second, if the contractor submits a proposal that lacks sufficient information to demonstrate support in a specific area, the Agency can then indicate how the proposal does not fulfill the need as stated in the request.

Listed below is an example of some factors and weights that an Agency might establish before an RFP is distributed:

Description	Weight
Factor I . . . .Technical Merit	25
Factor II . . .Proposer's Past Performance	25
Factor III . . .Understanding of the Requirements	15
Factor IV . .Adequacy and Suitability of Laboratory Equipment and Resources	15
Factor V . . .Academic Qualifications and Experience of Personnel	10
Factor VI . .Proposer's Related Experience	10

The format presented above assigns relative weights for each factor—with greater weight given to more important elements of the proposal. Technical merit (Factor I) includes technical merit, method validation and the ability to meet the MQOs, etc. Factor II includes how well the proposer performed in previous projects or related studies. A proposer's understanding (Factor III) is demonstrated by the laboratory's programs, commitments as well as certifications, licenses, etc., to ensure the requirements of the RFQ will be met. Adequacy and suitability (Factor IV) is generally an indication that the laboratory is presently situated to accept samples and conduct the work as proposed. Factor V focuses on topics covered previously in Section E.4.2 while the proposer's experience (Factor VI) is considered in Section E.4.7.

An Agency may use a Technical Evaluation Sheet—in conjunction with the Proposal Evaluation Plan as outlined in the next section (Table E.6)—to list the total weight for each factor and to provide a space for the evaluator's assigned rating. The evaluation sheet also provides areas to record the RFP number, identity of the proposer, and spaces for total score, remarks, and

evaluator's signature. The scoring and evaluation scheme is based on additional, more detailed, considerations which are briefly discussed in the next three sections (E.5.3.1 to E.5.3.3)

E.5.3.1 Review of Technical Proposal and Quality Manual

Each bidding-contractor laboratory will be asked to submit a technical proposal and a copy of its Quality Manual. This document is intended to address all of the technical and general laboratory requirements. The proposal and Quality Manual are reviewed by members of the TEC who are both familiar with the proposed project and are clearly knowledgeable in the field of radiochemistry.

Table E.6 is an example of a Proposal Evaluation Plan (based on information from the U.S. Geological Survey). This type of evaluation can be applied to proposals as they are considered by the TEC.

TABLE E.6 — Example of a Proposal Evaluation Plan

Proposal Evaluation

Objective: To ensure impartial, equitable, and comprehensive evaluation of proposals from contractors desiring to accomplish the work as outlined in the Request for Proposals and to assure selection of the contractor whose proposal, as submitted, offers optimum satisfaction of the government's objective with the best composite blend of performance, schedules, and cost.

Basic Philosophy: To obtain the best possible technical effort which satisfies all the requirements of the procurement at the lowest overall cost to the government.

Evaluation Procedures

1. Distribute proposals and evaluation instructions to Evaluation Committee.
2. Evaluation of proposals individually by each TEC member. Numerical values are recorded with a concise narrative justification for each rating.
3. The entire committee by group discussion prepares a consensus score for each proposal. Unanimity is attempted, but if not achieved, the Chairperson shall decide the score to be given.
4. A Contract Evaluation Sheet listing the individual score of each TEC member for each proposal and the consensus score for the proposal is prepared by the Chairperson. The proposals are then ranked in descending order.
5. The Chairperson next prepares an Evaluation Report which includes a Contract Evaluation Sheet, the rating

sheets of each evaluator, a narrative discussion of the strong and weak points of each proposal, and a list of questions which must be clarified at negotiation. This summary shall be forwarded to the Contracting Officer.

6. If required, technical clarification sessions are held with acceptable proposers.

7. Analysis and evaluation of the cost proposal will be made by the Contracting Officer for all proposals deemed technically acceptable. The Chairperson of the TEC will perform a quantitative and qualitative analysis on the cost proposals or those firms with whom cost negotiations will be conducted.

Evaluation Criteria

The criteria to be used in the evaluation of this proposal are selected before the RFP is issued. In accordance with the established Agency policy, TEC members prepare an average or consensus score for each proposal on the basis of these criteria and only on these criteria.

A guideline for your numerical rating and rating sheets with assigned weights for each criteria are outlined next under Technical Evaluation Guidelines for Numerical Rating.

Technical Evaluation Guidelines for Numerical Rating

1. Each item of the evaluation criteria will be based on a rating of 0 to 10 points. Therefore, each evaluator will score each item using the following guidelines:

   a. *Above normal*: 9 to 10 points (a quote element which has a high probability of exceeding the expressed RFP requirements).

   b. *Normal*: 6 to 8 points (a quote element which, in all probability, will meet the minimum requirements established in the RFP and Scope of Work).

   c. *Below normal*: 3 to 5 points (a quote element which may fail to meet the stated minimum requirements, but which is of such a nature that it has correction potential).

   d. *Unacceptable*: 0 to 2 points (a quote element which cannot be expected to met the stated minimum requirements and is of such a nature that drastic revision is necessary for correction).

2. Points will be awarded to each element based on the evaluation of the quote in terms of the questions asked.

3. The evaluator shall make no determination on his or her own as to the relative importance of various items of the criteria. The evaluator must apply a 0 to 10 point concept to each item without regard to his or her own opinion concerning one item being of greater significance than another. Each item is given a predetermined weight factor in the Evaluation Plan when the RFP is issued and these weight factors must be used in the evaluation.

812 E.5.3.2 Review of Laboratory Accreditation

813 A copy of the current accreditation(s) should be submitted with the proposal. The Agency should
814 confirm the laboratory's accreditation by contacting the Federal or State Agency that provided
815 the accreditation. In some cases, a public listing or code number is provided. Confirming that a
816 specific code number belongs to a given laboratory will require contacting the Agency that issued
817 the code.

818 E.5.3.3 Review of Experience

819 The laboratory should furnish references in relation to its past or present work (Section E.4.7.1).
820 To the extent possible, this should be done with regard to contracts or projects similar in
821 composition and size to the proposed project. One or more members of the TEC are responsible
822 for developing a list of pertinent questions and then contacting each reference listed by the
823 proposer. The answers obtained from each reference are recorded for use later in the evaluation
824 process. In some cases, the laboratory's previous performance for the same Agency should be
825 given special consideration.

826 **E.5.4 Pre-Award Proficiency Samples**

827 Some agencies may elect to send proficiency or performance testing (PT) samples to the
828 laboratories that meet a certain scoring criteria in order to demonstrate the laboratory's analytical
829 capability. The composition and number of samples should be determined by the nature of the
830 proposed project. The PT sample matrix should be composed of well-characterized materials. It
831 is recommended that site-specific PT matrix samples or method validation reference material
832 (MVRM; Chapter 6) be used when available. The matrix of which the PT sample is composed
833 must be well characterized and known to the Agency staff who supply the sample to the
834 candidate laboratory. For example, if an Agency is concerned with drinking water samples, then
835 the Agency's laboratory may use its own source of tap water as a base for making PT samples.
836 This water, with or without additives, may be supplied for this purpose.

837 Each competing lab should receive an identical set of PT samples. The RFP should specify who
838 will bear the cost of analyzing these samples, as well as the scoring scheme, (e.g., pass/fail) or a
839 sliding scale. Any lab failing to submit results should be automatically disqualified. The results
840 should be evaluated and each lab given a score. This allows the Agency to narrow the selection
841 further—after which only two or three candidate laboratories are considered.

842 At this point, two additional selection phases remain. A visit to each candidate's facilities comes
843 next (Section E.5.5) and thereafter, once all technical considerations are reviewed, the cost of the
844 contractor's service is examined last (Section E.5.6).

845 **E.5.5 Pre-Award Audit**

846 A pre-award audit, which may be an initial audit, is often performed to provide assurance that a
847 selected laboratory is capable of performing the required analyses in accordance with the SOW.
848 In other words, *is the laboratory's representation (proposal) realistic when compared to the*
849 *actual facilities?* To answer this question, auditors will be looking to see that a candidate
850 laboratory appears to have all the required elements to meet the proposed contract's needs. In
851 some cases, it may be appropriate to conduct both a pre-award audit, followed by an evaluation
852 after the work begins (see Section E.6.7 for information on ongoing laboratory evaluations).

853 The two or three labs with the highest combined scores (for technical proposals and proficiency
854 samples) may be given an on-site audit.

855 The pre-award audit is a key evaluating factor that is employed before the evaluation committee
856 makes a final selection. Many Federal agencies, including DOE, EPA, and USGS, have
857 developed forms for this purpose. Some of the key items to observe during an audit include:

858 • Sample Security – Will the integrity of samples be maintained for chain of custody? If
859 possible, examine the facility's current or past chain-of-custody practice.

860 • Methods – Are copies of SOP's available to every analyst? In some cases, one may check
861 equations used to identify and quantitate the radionuclides of interest. Additional concerns
862 include the potential for interferences, total propagated uncertainty, decision levels, and
863 minimum detectable concentrations.

864 • Method Validation Documentation – Verify the method validation documentation provided
865 in the response to the RFP. Have there been any QA/QC issues related to the methods? Are
866 the identified staff (provided in the RFP) qualified to perform the methods?

867 • Adherence to SOPs – This may include looking to see that sample preparation, chemical
868 analysis, and radiometric procedures are performed according to the appropriate SOP.

869 • Internal QC – Check the files and records.

- External QC/PT samples – Check files and records pertaining to third-party programs.

- Training – Check training logs. Examine analysts' credentials, qualifications, and proficiency examination results.

- Instrumentation – Check logs. Are instruments well maintained, is there much down time, are types and numbers listed in technical proposal correct? Look for QC chart documentation.

- Instrumentation – Calibration records. Do past and current calibration records indicate that the laboratory's instruments are capable of providing data consistent with project needs? Look at instrumentation characteristics, including resolution, detection efficiency, typical detection limits, etc. Are NIST-traceable materials used for detector calibration and chemical yield determinations?

- Personnel – Talk with and observe analysts. Verbal interaction with laboratory staff during an audit helps auditors to locate the information and likewise provide evidence for the knowledge and understanding of persons who conduct work in the candidate laboratory.

- Log-In – Is this area well-organized to reduce the possibility of sample mix-ups?

- Tracking – Is there a system of tracking samples through the lab?

Information about each laboratory may be gathered in various ways. One option available to the Agency is to provide each candidate laboratory with a list of questions or an outline for information that will be collected during the audit (Table E.7). The Agency's initial contact with the laboratory can include a packet with information about the audit and questions that the laboratory must address prior to the Agency's on-site visit. For example, from the checklist presented in Table E.7, one can see the laboratory will be asked about equipment. In advance of the audit, laboratory personnel can create a listing of all equipment or instruments that will be used to support the contract. Table E.7 also indicates information to be recorded by the auditors during the visit. The audit record includes the Agency's on-site observations, along with the laboratory's prepared responses.

TABLE E.7— Sample Checklist for Information Recorded During a Pre-Award Laboratory Audit

Laboratory:
Date:
Auditors:
1.
2.

A. Review packet that was sent to laboratory for completion:
   1. Laboratory Supervisor
   2. Laboratory Director
   3. Current Staff
   4. Is the laboratory responsible for all analyses? If not, what other laboratory(s) is (are) responsible?
   5. Agency responsible for [drinking water] program in the State.
   6. Does the laboratory perform analyses of environmental samples around nuclear power facilities, or from hospitals, colleges, universities, or other radionuclide users?
   7. Agency responsible for sample collections in item 6.

B. Laboratory Facilities:
   1. Check all items in the laboratory packet.
   2. Comments
   3. Is there a Hot Laboratory or a designated area for samples from a nuclear power facility that would represent a nuclear accident or incident? Is this documented in the SOP or QA Manual?

C. Laboratory Equipment and Supplies:
   1. Check all items on the laboratory packet. Includes analytical balances, pH meters, etc.
   2. Comments
   3. Radiation counting instruments:
      a. Thin window gas-flow proportional counters
      b. Windowless gas-flow proportional counters
      c. Liquid scintillation counter
      d. Alpha scintillation counter
      e. Radon gas-counting system
      f. Alpha spectrometer
      g. Gamma spectrometer systems:
         1. Ge (HPGe) detectors
         2. NaI detectors
         3. Multichannel analyzer(s)

D. Analytical Methodology:
   1. Check all items on the laboratory packet.
   2. Comments

E. Sample Collection, Handling, and Preservation:
   1. Check all items on the laboratory packet.
   2. Comments

F. Quality Assurance Section:
   1. Examine laboratory SOP
      a. Comments

   2. Examine laboratory's Quality Manual
      a. Comments

3. Performance Evaluation Studies (Blind)
    a. Comments and results

4. Maintenance records on counting instruments and analytical balances.
    a. Comments and results

5. Calibration data
    a. Gamma Spectrometer system
        1. Calibration source
        2. Sufficient energy range
        3. Calibration frequency
        4. Control charts
            a. Full Peak Efficiency
            b. Resolution
            c. Background

    b. Alpha/Beta counters
        1. Calibration source
        2. Calibration frequency
        3. Control charts
            a. Alpha
            b. Beta
            c. Background

    c. Radon counters
        1. Calibration source
        2. Frequency of radon cell background checks

    d. Liquid Scintillation Analyzer
        1. Calibration sources
        2. Calibration frequency
        3. Control charts
            a. H-3
            b. C-14
            c. Background
            d. Quench

6. Absorption and Efficiency curves:
    a. Alpha absorption curve
    b. Beta absorption curve
    c. Ra-226 efficiency determination
    d. Ra-228 efficiency determination
    e. Sr-89, Sr-90, and Y-90 efficiency determinations
    f. Uranium efficiency determination

7. Laboratory QC Samples
    a. Spikes
    b. Replicates/duplicates
    c. Blanks
    d. Cross check samples
    e. Frequency of analysis
    f. Contingency actions if control samples are out of specification
    g. Frequency of analysis

E. Records and Data Reporting
    1. Typical data package
    2. Electronic data deliverable format
    3. Final data report

H. Software Verification and Validation
    1. Instrumentation and Equipment Control and Calibrations
    2. Analytical Procedure Calculations/Data Reduction
    3. Record Keeping/Laboratory/Laboratory Information Management System/Sample Tracking
    4. Quality Assurance Related — QC sample program/instrument QC

E.5.6 Comparison of Prices

To this point, the selection process focuses on technical issues related to conducting work under the proposed contract. Keeping this separate from cost considerations simplifies the process and helps to sustain reviewer objectivity. Once the scoring of labs is final, the price of analyses may be reviewed and compared. Prices are now considered along with inspection results. This part of the process is best performed by technical personnel, including members of the TEC who work in either a laboratory or the field setting, and who possess the knowledge to recognize a price that is reasonable for a given type of analysis. Various scenarios may apply where prices differ:

- Candidates are dropped generally if their proposed prices are extreme.

- Laboratories that score well—aside from their prices that may still be on the high side—are given an opportunity to rebid with a best and final cost. This lets laboratories know they have entered the final stage of the selection process.

A final ranking is based on the technical evaluation, including the proficiency examination and audit if conducted, and the best-and-final prices submitted by each laboratory.

While there is no way to determine how evaluations may be conducted in the future, some extra consideration may be given to proposals that offer greater technical capabilities (i.e., those that

house state-of-the-art or high-tech analytical services) as opposed to fulfilling the minimum requirements of the RFP.

E.5.7 Debriefing of Unsuccessful Vendors

At an appropriate time in the selection process, all unsuccessful bidders are sent a letter outlining the reasons that they were not awarded the contract. As noted previously, the RFP should be very explicit in illustrating what a proposal should contain and which areas carry more or less weight with regard to the Agency's evaluation. If so, the Agency is able to provide a written response to specifically identify areas of the proposal where the contractor lacks the appropriate services or is apparently unable to present a sufficiently strong case documenting an ability to do the work. Also, as stated previously, the proposer must present as clear a case as possible and write into the proposal all relevant information. A simple deletion of key information will put a capable proposer out of the running in spite of the experience, support, and services they are able to render an Agency.

If a contractor wishes an individual debriefing, the Agency can arrange to have the TEC meet with the contractor's representatives. This meeting allows for an informal exchange to further explore issues to the satisfaction of the proposer. This exchange may offer the Agency an opportunity to restate and further clarify the expected minimum qualifications that are required of the proposer.

A more formal approach contesting the Agency's decision follows after a protest is lodged by the contractor. In this case, the Agency's TEC and the contractor's representatives are accompanied by legal council for both sides.

E.6 The Award

The selection process ends when the Agency personnel designate which contractor will receive the award. Several steps follow in advance of formally presenting the award. This essentially includes in-house processing, a review by the Agency's legal department, and a final review by the contract staff. These activities verify that the entire selection process was followed properly and that the contract's paperwork is correct. The Agency's contracts office then signs the proper documents and the paperwork is sent to the contractor. The contract becomes effective as of the date when the government's contracting officer signs.

E.7 For the Duration of the Contract

After the award is made, the Agency enters into a working relationship with the contract laboratory and work begins. Over the period of the contract, the Agency will send samples, receive deliverables, and periodically check the laboratory's performance. The work according to the SOW and the activities associated with performance checks and laboratory evaluations are topics covered beginning with the next section. Furthermore, as data are delivered to the Agency, invoices will be sent by the contractor to the Agency. The Agency will process the invoices in steps: that receipt of data is initially confirmed, the results are appropriate (i.e., valid), and finally that the invoice is paid. This activity may occur routinely as invoices arrive—weekly, monthly, or at some other time interval throughout the course of a contract.

Keep in mind that the structured planning process is iterative in nature and may come into play at any point during a contract period. For example, Federal or State laboratories engaging contract-support services may be involved in routine monitoring of numerous sampling sites. For sets of samples that are repeatedly taken from a common location over the course of years, only the discovery of unique results or change in performance-based methods may instigate an iteration and a review of the MQOs. For other types of projects, such as a location undergoing a MARSSIM-site survey, the project plan may change as preliminary survey work enters a period of discovery—e.g., during a scoping or characterization survey (MARSSIM, 2000). Even during a final status survey, discovery of some previously unknown source of radioactive contamination may force one to restate not only the problem, but to reconsider every step in the planning process. Modification of a contract may be necessary to address these circumstances.

E.7.1 Managing a Contract

Communication is key to the successful management and execution of the contract. Problems, schedule, delays, potential overruns, etc., can only be resolved quickly if communications between the laboratory and Agency are conducted promptly.

A key element in managing a contract is the timely verification (assessment) of the data packages provided by the laboratory. Early identification of problems allows for corrective actions to improve laboratory performance and, if necessary, the cessation of laboratory analyses until solutions can be instituted to prevent the production of large amounts of data which are unusable. Note that some sample matrices and processing methods can be problematic for even the best laboratories. Thus the contract manager must be able to discern between failures due to legitimate reasons and poor laboratory performance.

E.7.2 Responsibility of the Contractor

First and foremost, the responsibility of the laboratory is to meet the performance criteria of the contract. If the SOW is appropriately written, this provides guidance necessary to ensure the data produced will meet the project planning goals and be of definable quality. Likewise, the laboratory must communicate anticipated or unforeseen problems as soon as possible. Again, this could easily occur with complex, unusual, or problematic sample matrices. Communication is vital to make sure that matrix interferences are recognized as early as possible, and that subsequent analyses are planned accordingly.

The laboratory's managers must plan the analysis—that is, have supplies, facilities, staff, and instruments available as needed—and schedule the analysis to meet the Agency's due date. In the latter case, a brief buffer period might be included for unanticipated problems and delays, thus allowing the laboratory the opportunity to take appropriate corrective action on problems encountered during an analysis.

E.7.3 Responsibility of the Agency

During the period of the contract, the Agency is responsible for employing external quality assurance oversight. Thus the performance of the laboratory should be monitored continually to insure the Agency is receiving compliant results. Just because a laboratory produces acceptable results at the beginning of its performance on a contract does not necessarily mean that it will continue to do so throughout the entire contract period. For example, the quality of the data can degenerate at times when an unusually heavy workload is encountered by an environmental laboratory. One way to monitor this performance is to review the results of internal and external quality assurance programs. This may in part take the form of site visits (including onsite audits), inclusion of QC samples, evaluation of performance in Performance Evaluations or intercomparison programs, desk audits, and data assessments.

E.7.4 Anomalies and Nonconformance

The contractor must document and report all deviations from the method and unexpected observations that may be of significance to the data user. Such deviations should be documented in the narrative section of the data package produced by the contract laboratory. Each narrative should be monitored closely to assure that the laboratory is documenting departures from contract requirements or acceptable practice. The Agency's reviewer should assure that the reason(s) given for the departures are clearly explained and are credible. The repeated reporting of the same deviation may be an indication of internal laboratory problems.

E.7.5 Laboratory Assessment

As work under a contract progresses over time, there are two principle means to assess a laboratory's performance: by having the laboratory process quality control samples (Section E.7.5.1 and E.7.5.2), and by Agency personnel visiting the laboratory to conduct on-site evaluations (Section E.7.5.3).

E.7.5.1 Performance and Quality Control Samples

A laboratory's performance is checked in one of several ways, including the use of Agency QC samples, the laboratory's QC samples, laboratory participation in a performance evaluation program, Agency certification program, and through Agency audits, which may include an on-site visit.

There are several approaches to determining that an analysis is accurate and that the data reflect a true result. One check on each analysis comes from the laboratory's own QC measures. The contractor will routinely run standards, prepared spiked samples, and blanks, along with the samples submitted by the Agency. Calibrations are also performed and a laboratory technician is expected to record information to document instrument performance.

Another avenue for QC comes with measures taken by the Agency, including the incorporation of a number of double-blind samples, with each batch of samples sent to the contract laboratory. The preparation of double-blind samples for matrices other than water is difficult. A sample designated as a *blind sample* is one that the contractor knows is submitted by the Agency for QC purposes. A *double-blind sample* is presented to the laboratory as if it were just another sample with no indication that this is for QC purposes. In the former case, the samples may be labeled in such a manner that the laboratory recognizes these as QC samples. In the latter case, unless the Agency takes steps to use very similar containers and labeling as that for the field samples, the laboratory may recognize the double-blind samples for what they are. This in effect compromises the use of a double-blind sample. In each case, the Agency knows the level or amount of each radionuclide in the blind sample.

When the analysis for a set of samples is complete and data are sent to the Agency, the Agency in turn checks the results for the QC samples and then performs data validation. In the case of characterization studies, one may continue to check results for QC samples, but data validation packages may not be required. If the double-blind results are not within reasonable limits, the Agency will need to examine how these specific data may indicate a problem. In the meantime, work on subsequent sample sets cannot go forward until the problem is resolved. Some or all

samples in the questionable batch may need to be reanalyzed depending on the findings for the QC samples. This is a case where storage of samples by the laboratory—e.g., from three to six months after analyses are performed—allows the Agency to back track and designate specific samples for further or repeated analyses. The one exception to going back and doing additional analyses arises for samples containing radionuclides with short half lives. This type of sample requires a more immediate assessment to allow for repeated analyses, if needed.

Where data validation is required, the Agency will routinely look at results for the QC samples that are added to the sample sets collected in the field. An additional QC measure includes a routine examination—for example, on a monthly or quarterly basis—of the laboratory's results for their own internal QC samples. This includes laboratory samples prepared as spikes, duplicates, and blanks that are also run along with the Agency samples.

The Agency can also schedule times to monitor a contractor laboratory's participation in a performance evaluation program—for example, those supported by the DOE, EPA, NIST, or NRC. Each laboratory, including the Agency's own facilities, are expected to participate in such programs. The Agency will also check to see if a laboratory's accreditation (if required) is current and this is something that should be maintained along with participation in a Federally sponsored performance evaluation program. In general, the States accredit laboratories within their jurisdiction.

E.7.5.2 Laboratory Performance Evaluation Programs

Participating in a collaborative interlaboratory testing program (such as the PT programs mentioned in E.5.4) is the best way for a laboratory to demonstrate or an Agency to evaluate a laboratory's measurement quality in comparison to other laboratories or to performance acceptance criteria. Furthermore, because MARLAP promotes consistency among radiochemistry laboratories, it is scientifically, programmatically, and economically advantageous to embrace the concept of a common basis for radioanalytical measurements—a measurement quality system that is ultimately linked to the national physical standards. ANSI N42.23, *Measurement and Associated Instrument Quality Assurance for Radioassay Laboratories*, defines a system in which the quality and traceability of service laboratory measurements to the national standards can be demonstrated through reference (and monitoring) laboratories. The service (in this case the contracted) laboratory shall analyze NIST traceable reference performance testing materials to examine the bias and precision of an analytical methodology or an analyst. Traceable reference material, a sample of known analyte concentration, is prepared from NIST Standard Reference Material or derived reference material supplied by a NIST traceable radioactive source

manufacturer (ANSI N42.22). Demonstration of measurement performance and traceability shall be conducted at an appropriate frequency.

E.7.5.3 Laboratory Evaluations Performed During the Contract Period

An audit before awarding a contract emphasizes an examination of availability of instruments, facilities, and the potential to handle the anticipated volume of work. This also includes recognizing that the proper personnel are in place to support the contract. After the award, a laboratory evaluation will place additional weight on how instruments and personnel are functioning on a daily basis. Thus, logbooks, charts, or other documentation that are produced as the work progresses are now examined. This type of evaluation during the contract period uses an approach that differs from the pre-award audit (Section E.5.5). The format and documentation for an on-site audit may differ from Agency to Agency. An Agency may wish to examine the EPA forms (EPA, 1997b) and either adopt these or modify them to accommodate radionuclide work that includes sample matrices other than water or additional nuclides not presently listed.

There are two types of evaluations or audits that can be performed during the life of a contract. The first involves Agency personnel that visit the contractor's facilities. The second approach includes activities conducted by Agency personnel without visiting the laboratory.

In the former case, Agency personnel examine documentation at the laboratory, including each instrument's logbook which is used to record background values, or to ensure that QC charts are current. During this type of evaluation, the Agency and contractor personnel have an opportunity to communicate face-to-face, which is a benefit to both parties when clarification or additional detail is needed. For example, this audit's goal essentially is to check the capability of the laboratory to perform the ongoing work according to the contract work. In this case, an auditor may request to see one or more data packages, and then follow the information described in each package—including such items as sample tracking and documentation concerning sample preparation and analysis—to verify that the laboratory is now accomplishing the work as described by the SOW and in conformance with the Quality Manual.

In the latter case, one conducts what might be called a *desk audit*, where Agency personnel review the contract and examine records or documentation that have come in as part of the project's deliverables. For the most part, the Agency should constantly be monitoring activities under the contract, and in this sense, a desk audit is a daily activity without a formal process being applied at any specific point in time. However, depending on the Agency's practice, if on-site visits are not made, then a desk audit becomes the only means to track activities under the contract. One approach to a desk audit is thus a periodic review—for example, every 6 or 12

months—of QC records to track the laboratory's performance over that period of time. This allows the Agency to determine if there are deviations, shifts, or other trends that appear over time.

Each evaluation presents an additional opportunity to monitor various laboratory parameters, such as turnaround time. This is most important in cases when samples contain radionuclides having short half lives. During an on-site evaluation, the Agency is able to determine if additional emphasis is required to tighten the time frame between sample receipt and analysis. The personal interaction between Agency and laboratory permits a constructive dialog and facilitates an understanding of the possible means to increase or maintain the efficiency when processing and analyzing samples at the contractor's facility.

E.8 Contract Completion

There are several general areas of concern at the close of a contract that may be addressed differently depending on the Agency or nature of the project under a given contract. For example, Agency personnel who monitor contracts will review invoices to be certain that work is complete and that the corresponding results are considered acceptable. Once such monitoring activity provides the proper verification that the work is complete, then the Agency's financial office processes all related bills and makes final payment for the work.

The laboratory should send in final deliverables, including routine submissions of raw data or records, as is the practice under the contract. Also, when applicable, Agency-owned equipment shared with the laboratory during the contract period will be returned. The disposition of samples still in storage at the contractor's facility and additional records or other raw data must be decided and specified. The Agency may wish to receive all or part of these items—otherwise, disposal of sample materials and documents held by the contractor must be arranged.

In some cases, work under the contract may create conditions where more time is necessary to process samples that remain or to process additional work that arises during the latter part of the contract period. Depending on the Agency, funding, nature of the project, or other factor, the contract may be extended for a period of time, which may vary from weeks to months. Otherwise, once the contract comes to a close, the work ceases.

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U.S. Code of Federal Regulations, Title 10, Part 30, *Rules of General Applicability to Domestic Licensing of Byproduct Material.*

APPENDIX F LABORATORY SUBSAMPLING

F.1 Introduction

In most cases a sample that arrives at the laboratory cannot be analyzed in its entirety. Usually only a small subsample is taken for analysis, and the analyte concentration of the subsample is assumed to be approximately equal to that of the sample itself. Obviously a subsample cannot be perfectly representative of a heterogeneous sample. Improper subsampling may introduce a significant bias into the analytical process. Even when done properly, subsampling increases the variability of the measured result. There are simple methods for controlling the bias, but estimating and controlling the random variability is less straightforward.

French geologist Pierre Gy has developed a theory of particulate sampling for applications in mining exploration and development (Gy, 1992), and his work has been promoted in the United States by Francis Pitard (Pitard, 1993). The basic concept of the theory is that the variability in the analyte concentration of a laboratory sample depends on the mass of the sample and the distribution of particle types and sizes in the material sampled. The particulate sampling theory developed by Gy is applicable to the sampling of soils and radioactive waste (EPA 1992a, 1992b). In this appendix, the theory is applied in qualitative and quantitative approaches to the subsampling of particulate solids in the radiation laboratory.

There are many examples of the use of Gy's theory in the mining industry (Assibey-Bonsu 1996; Stephens and Chapman, 1993; Bilonick, 1990; Borgman et al., 1996), and a computer program has been developed for its implementation (Minkkinen, 1989). The theory has recently been adapted for use in environmental science. To date, most environmental applications have been in laboratory and field sampling for hazardous chemicals in Superfund cleanups (Borgman et al., 1994; Shefsky 1997), and there are several applications of the theory that involve mixed radioactive and hazardous wastes (Tamura, 1976).

In principle, particulate sampling theory applies to materials of any type, since even gases and liquids are composed of particles (molecules). However, sampling large numbers of randomly distributed molecules in a fluid presents few statistical difficulties; so, the theory is more often applied to particulate solids.

One of the most likely applications of Gy's theory in the radiation laboratory is the subsampling of soils. Natural soils are complex mixtures of different particle types, shapes, densities, and sizes. Soil particles range from fine clays at less than 4 μm diameter to coarse sand that ranges over 2 mm in diameter, spanning about 4 orders of magnitude. Contaminants may be absorbed or chemically combined into the soil matrix, adsorbed onto the surfaces of particles, or may occur in

discrete particles that are not bound to the soil matrix. Contaminant particles in soil can vary in size from fine airborne deposits of less than 1 μm diameter to relatively large pellets. These factors and others, including radionuclide half-lives, significantly affect the sampling problem.

F.2 Basic Concepts

This appendix applies Gy's sampling theory to subsampling. To avoid confusion, the terms "lot" and "sample" will be used here instead of "sample" and "subsample," respectively. There may be several subsampling stages at the laboratory, and all of the stages must be considered. At any stage of sampling, the *lot* is the collection of particles from which a portion is to be taken, and the *sample* is the portion taken to represent the lot.

In Gy's theory, the chemical or physical component whose proportion in a lot is of interest is called the *critical component*. In the context of radiochemistry, the critical component may be a radionuclide, but, if the chemical form of the radionuclide is known, it may be more useful to consider the critical component to be a chemical compound. Certain applications of Gy's theory require knowledge of the density, so the physical form of the compound may also be important. In the limited context of this appendix, however, the critical component will be identified with the *analyte*, which is usually a radionuclide.

The proportion of critical component by mass in a lot, sample, or particle is called the *critical content*. In the context of radiochemistry, the critical content is directly related to the activity concentration, or massic activity, of the analyte, but it is expressed as a dimensionless number between 0 and 1. Many of the mathematical formulas used in Gy's sampling theory are equally valid if the critical content is replaced everywhere by analyte concentration. All the formulas in this appendix will be expressed in terms of analyte concentration, not critical content.

The *sampling error* of a sample S is defined, for our purposes, as the relative error in the analyte concentration of the sample, or $(z_S - z_L) / z_L$, where z_S is the analyte concentration of the sample and z_L is the analyte concentration of the lot. If the sample is the entire lot, the sampling error is zero by definition.

A lot may be heterogeneous with respect to many characteristics, including particle size, density, and analyte concentration. Of these, analyte concentration is most important for the purposes of this appendix. A lot may be considered perfectly homogeneous when all particles have the same concentration of analyte.

The term "heterogeneity" is commonly used with more than one meaning. Gy attempts to clarify the concepts by distinguishing between two types of heterogeneity. The *constitution 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. The *distribution heterogeneity* of a lot depends not only on the variations among particles but also on their spatial distribution.[1] Thus, the distribution heterogeneity may change, for example, when the material is shaken or mixed. In Gy's theory, both constitution heterogeneity and distribution heterogeneity are quantitative terms, which are defined mathematically.

Heterogeneity is also sometimes described as either "random" or "nonrandom" (ASTM D5956). *Random heterogeneity* is exhibited by well-mixed material, in which dissimilar particles are randomly distributed. *Nonrandom heterogeneity* occurs when particles are not randomly distributed, but instead are stratified. There is a natural tendency for a randomly heterogeneous lot to become more stratified when shaken, bounced, or stirred. The same material may exhibit both random and nonrandom heterogeneity at different times in its history.[2]

In MARLAP's terminology, the *representativeness* of a sample denotes the closeness of the analyte concentration of the sample to the analyte concentration of the lot. A sample is representative if its analyte concentration is close to the concentration of the lot, just as a measured result is accurate if its value is close to the value of the measurand. Representativeness may be affected by bias and imprecision in the sampling process, just as accuracy may be affected by bias and imprecision in the measurement process.[3]

The concept of representativeness is related to the question of heterogeneity. If a lot is completely homogeneous, then any sample is perfectly representative of the lot, regardless of the sampling strategy, but as the degree of heterogeneity increases, it becomes more difficult to select a representative sample.

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[1]ASTM D5956 uses the terms "compositional heterogeneity" and "distributional heterogeneity."

[2]A state of random heterogeneity exists when the distribution heterogeneity is zero. A state of nonrandom heterogeneity exists when the distribution heterogeneity is positive.

[3]The term "representativeness" is also like "accuracy" inasmuch as it is used with different meanings by different people. The definition provided here is MARLAP's definition.

F.3 Sources of Measurement Error

The total variance of the result of a measurement is the sum of the variances of a series of error components, including errors produced in the field and in the laboratory. Errors in the laboratory may be divided into those associated with sampling and those associated with sample preparation and analysis.

Note that the practical significance of any error, including sampling error, depends on its magnitude relative to the other errors. If a crude analytical procedure is used or if there is a relatively large counting uncertainty, the sampling error may be relatively unimportant. In other cases the sampling error may dominate. If the standard uncertainty from either source is less than about one-third of the standard uncertainty from the other, the smaller uncertainty component contributes little to the combined standard uncertainty.

This appendix focuses only on sampling errors, which include the following:

- Sampling bias;
- The fundamental error; and
- Grouping and segregation errors.

The following sections define the three types of sampling errors and present methods for controlling or quantifying them. (See Chapter 19, *Measurement Statistics*, for a more general discussion of laboratory measurement errors.)

F.3.1 Sampling Bias

Sampling bias is often related to distribution heterogeneity. When there is a correlation between the physical properties of a particle and its location in the lot, care is required to avoid taking a biased sample. For example, if the analyte is primarily concentrated at the bottom of the lot, the analyte concentration of a sample taken from the top will be biased low. Situations like this may occur frequently in environmental radiochemical analysis, since non-natural radioactive materials often tend to be concentrated in the smallest particles, which tend to settle to the bottom of the container.

Sampling bias can be controlled by the use of "correct" sampling procedures. A sampling procedure is called "correct" if every particle in the lot has the same probability of being selected for the sample. As a practical rule, a sample is guaranteed to be unbiased only if the sampling procedure is correct.

> RULE 1: A sample is guaranteed to be unbiased only if every particle in the lot has the same probability of selection.

The preceding rule is not being followed, for example, if particles on the bottom or in recesses of the container are never selected.

Actually the rule stated above is only approximately true.[4] It is invalid if the sample consists of only a few particles, or if only a few particles in the lot contain most of the mass. Therefore, a second practical rule of sampling is that the sample must be many times larger (by weight) than the largest particle of the lot.

> RULE 2: The sample must be many times larger than the largest particle of the lot.

Grouping of particles should also be minimized. If the particles form clumps, the effective number of particles in the lot is actually the number of clumps.

F.3.2 Fundamental Error

When a sample is taken, the existence of constitution heterogeneity in a lot leads to an unavoidable sampling error, called the *fundamental error*. Its variance, called the *fundamental variance*, is a property of the lot and the size of the sample. It represents the smallest sampling variance that can be achieved without altering individual particles or taking a larger sample. The fundamental variance is not affected by homogenizing, or mixing, and exists even when the sampling procedure is correct. It cannot be eliminated, but it can be reduced either by increasing the size of the sample or by reducing the particle sizes before sampling (e.g., by grinding).

> RULE 3: The fundamental variance may be reduced by:
> - Taking a larger sample
> - Reducing the particle sizes before sampling

This theoretical minimum sampling variance is only achieved in practice when the lot is in a state of pure random heterogeneity (and the sampling is performed correctly). If there is nonrandom

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[4]A sample is unbiased if $E(Z_S / M_S) = z_L$, where Z_S is the total analyte activity in the sample, M_S is the sample mass, z_L is the analyte activity concentration of the lot, and $E()$ denotes expected value. Equal selection probabilities guarantee only that $E(Z_S) / E(M_S) = z_L$.

heterogeneity at the time of sampling, the total sampling variance will be larger than the fundamental variance.

Either method for reducing the fundamental variance may be difficult or costly to implement in some situations. When large objects or consolidated materials are contained in the lot, particle size reduction for every lot may be unrealistically expensive. Not all materials are amenable to particle size reduction (e.g., steel). If available, knowledge of the expected contamination types and distributions may be used to reduce the need for particle size reduction. For example, it may be known that large objects in the lot are relatively free of analyte. If so, then such objects might be removed or analyzed separately using different methods, depending on the project objectives.

When particle size reduction is required and trace levels of contamination are expected in the lot, complete decontamination of grinding or milling equipment is required to avoid the possibility of cross-sample contamination. The equipment should be constructed of non-contaminating materials that are compatible with the chemical components of the lot. Glass, ceramic and stainless steel are typical materials. Particle size reducers, such as ball mills and ceramic plate grinders, require dried samples and thorough decontamination. Mechanical splitters may be difficult to decontaminate. A grinding blank may be analyzed to check for contamination of the grinding equipment.

Contamination from airborne sources (e.g., stack releases or incinerator emissions), leaching (e.g., stored mill tailings), or from weathering of contaminated surfaces tends to be dispersed and deposited as many fine particles. In these cases, as long as the particles of the matrix are small relative to the sample size (Rule 2), grinding the material is unlikely to make dramatic differences in the fundamental variance, but the variance tends to be small because of the large number of contaminant particles.

If the lot contains only a few contaminant particles, all of which are very small, the fundamental variance may remain large even after extensive grinding. However, the analytical procedure may be amenable to modifications that permit larger samples to be processed. For example, dissolution of a large solid sample may be followed by subsampling of the solution to obtain the amount needed for further analysis. Since liquid solutions tend to be more easily homogenized than solids, subsampling from the solution contributes little to the total sampling error.

If neither reducing the particle size nor increasing the sample size is feasible, more innovative analytical techniques may have to be considered.

F.3.3 Grouping and Segregation Error

Since the analyte is often more closely associated with particles having certain characteristics (e.g., small or dense), it may become concentrated in one portion of the lot or in clumps spread throughout the lot. Such effects tend to increase distribution heterogeneity.

The existence of distribution heterogeneity leads to a sampling error called the *grouping and segregation error*. The grouping and segregation variance is not as easily quantified as the fundamental variance, but there are methods for reducing its magnitude.

Although the traditional approach to reducing the grouping and segregation error is mixing, or homogenizing, the material, Gy and Pitard warn that homogenizing heterogeneous materials is often difficult, especially if a large quantity is involved. Using improper methods, such as stirring, may actually tend to increase segregation, and, even if a degree of homogeneity is achieved, it is likely to be short-lived, because of the constant influence of gravity. Agitation of particulate matter during transport and handling also tends to produce segregation of particles by size, shape, and density. During these processes, the denser, smaller, and rounder particles tend to settle to the bottom of the container, while less dense, larger, and flatter particles tend to rise to the top.

> RULE 4: The effects of homogenizing heterogeneous solid material tend to be short-lived because of the constant influence of gravity. Denser, smaller, and rounder particles tend to settle to the bottom of a container, while less dense, larger, and flatter particles tend to rise to the top.

As an alternative to homogenizing, Gy and Pitard recommend sampling procedures to reduce not the distribution heterogeneity itself, but its effects on the grouping and segregation error. Gy classifies sampling procedures into two categories: (1) increment sampling, and (2) splitting. Increment sampling involves extracting a number of small portions, called *increments*, from the lot, which are combined to form the sample. Splitting involves dividing the lot into a large number of approximately equal-sized portions and recombining these portions into a smaller number of potential samples. One of the potential samples is then randomly chosen as the actual sample.

A sample composed of many increments will generally be more representative than a sample composed of a single increment. For example, if a 25 g sample is required, it is better to take five 5 g increments, selected from different locations in the sample, than to take a single 25 g increment.

206 RULE 5: A sample composed of many increments taken from different locations in the lot is
207 usually more representative than a sample composed of a single increment.

208 The variance reduction achievable by increment sampling depends on the distribution
209 heterogeneity of the lot. If the lot is in a state of pure random heterogeneity, increment sampling
210 provides no benefit. On the other hand, if the lot is highly stratified, the standard deviation of the
211 analyte concentration of a small composite sample formed from n independent increments may
212 be smaller by a factor of $1/\sqrt{n}$ than the standard deviation for a sample composed of a single
213 increment.[5] Variance reductions intermediate between these two extremes are most likely in
214 practice.

215 Figures F.1 and F.2 illustrate what Gy calls "increment delimitation error" and "increment
216 extraction error," respectively. One method for extracting increments is the one-dimensional
217 "Japanese slab-cake" method (Gy 1992, Pitard 1993). First, the material in the lot is spread out
218 into an elongated pile with roughly constant width and height. Then a scoop or spatula is used to
219 delimit and extract evenly spaced cross-sections from the pile. A flat-bottomed scoop should be
220 used for this purpose to avoid leaving particles at the bottom of the pile. Ideally it should also
221 have vertical sides, as shown in Figure F.3, although such scoops may not be commercially
222 available. If a spatula is used, its width must be much larger than the largest particles to be
223 sampled, since particles will tend to fall off the edges (see Figure F.2).

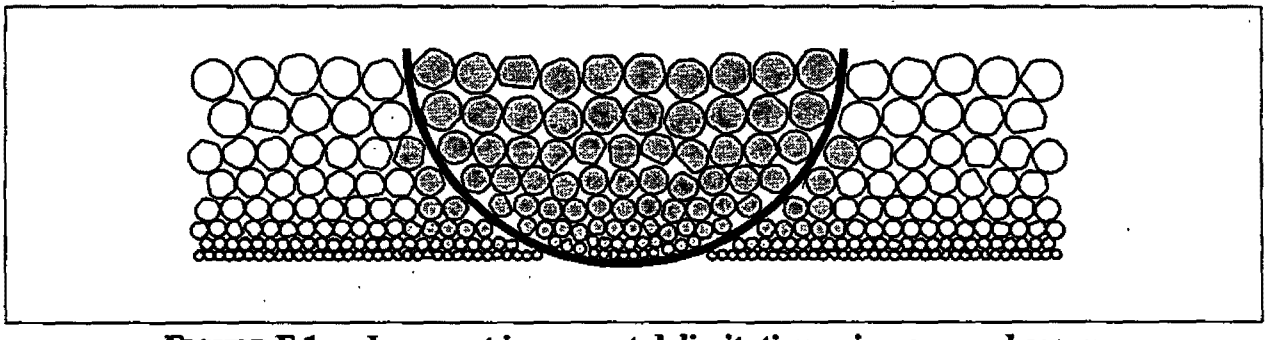

FIGURE F.1 — Incorrect increment delimitation using a round scoop

[5]This statement assumes the stratification is such that a single large increment is likely to have no more constitution heterogeneity than any of the n smaller increment.

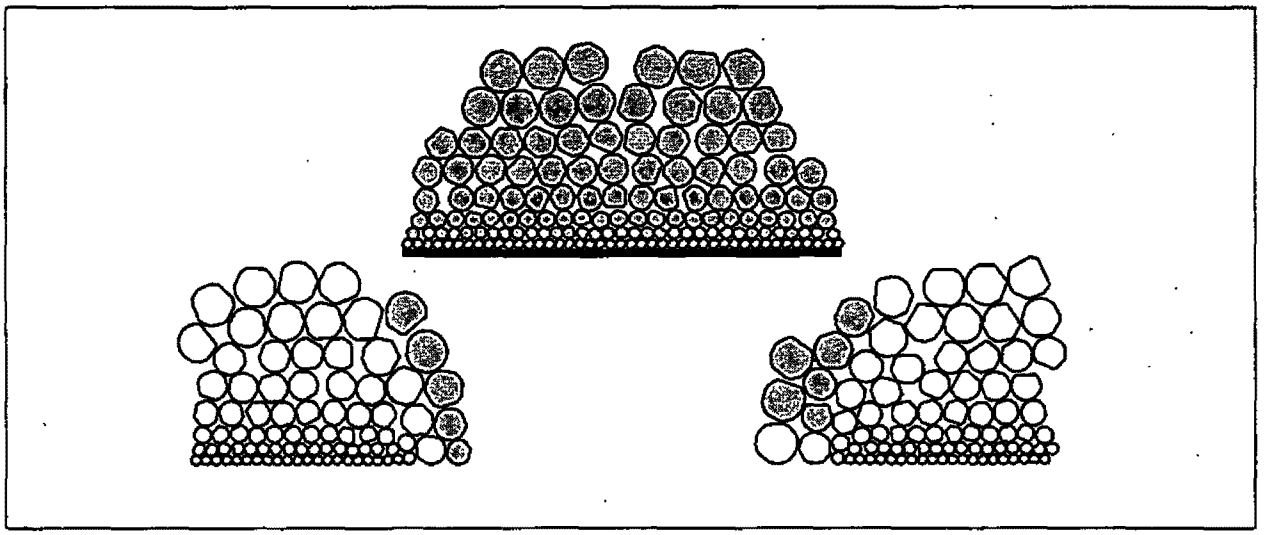

FIGURE F.2 — Incorrect increment extraction using a spatula

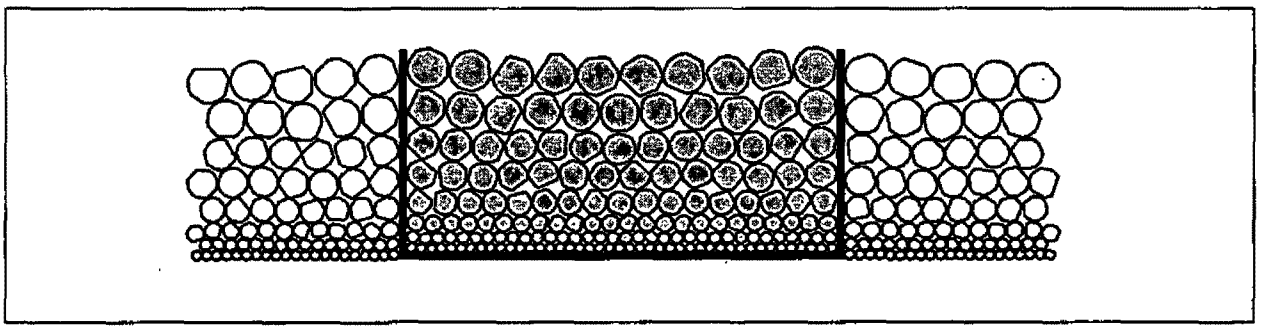

FIGURE F.3 — Correct increment delimitation using a rectangular scoop

Splitting may be performed correctly by mechanical splitters, such as riffle splitters and sectorial splitters, or it may be performed manually by "fractional shoveling" (or "fractional scooping" in the laboratory). Fractional shoveling involves removing small portions of equal size from the lot and depositing them into two or more empty containers (or piles), cycling through the containers in order, and repeating the process until all the material has been deposited. When this process is complete, one container is chosen at random to be the sample.

The traditional "coning and quartering" method for splitting, although correct, is not recommended because it produces a subsample from too few increments. With this method, the material is

mixed by forming it into a cone, adding a fraction of the sample at a time to the apex of the cone. After the entire sample is mixed in this way, the cone is flattened into a circular layer. Next the circular layer of material is divided into quarters and two opposite quarters are discarded. This process may be repeated until a suitable sample size is obtained (Shugar and Dean, 1990).

Homogenization may also be achieved with some types of grinding equipment, such as a ring-and-puck mill.

According to Gy, small quantities of solid material, up to a few kilograms, can be homogenized effectively in the laboratory. He recommends the use of a jar-shaker for this purpose and states that immediately after the lot is shaken, the sample may be taken directly from the jar using a spatula (Gy, 1992). Although Pitard recognizes the possibility of homogenizing small lots in the laboratory using a mechanical mixer that rotates and tumbles a closed container, he also states that homogenizing heterogeneous materials is often "wishful thinking" and recommends the one-dimensional Japanese slab-cake procedure instead (Pitard, 1993, §14.4.3).

F.4 Implementation of the Particulate Sampling Theory

DISCLAIMER: *Gy's theory is currently the best-known and most completely developed theory of particulate sampling, but the problem is a difficult one, and the mathematical approaches offered may not give satisfactory results for all purposes. Quantitative estimates of the fundamental variance are often crude. Conservative assumptions are sometimes needed to permit mathematical solutions of the equations, leading to upper bounds for the fundamental variance which may be significantly overestimated. It appears that the theory has not been applied previously to sampling for radiochemical analysis, and no data are available to demonstrate the limits of its applicability. Until such data are available, MARLAP recommends the theory only for crude estimation.*

F.4.1 The Fundamental Variance

Gy's sampling theory leads to the following equation for the fundamental variance σ^2_{FE} (Gy 1992, Pitard 1993):

$$\sigma^2_{FE} = \left(\frac{1}{M_S} - \frac{1}{M_L} \right) \sum_{i=1}^{N} \frac{(z_i - z_L)^2}{z_L^2} \frac{m_i^2}{M_L} \qquad \text{(F.1)}$$

Here

M_S is the mass of the sample (g)

M_L is the mass of the lot (g)
N is the number of particles in the lot
z_i is the analyte concentration of the i^{th} particle
z_L is the analyte concentration of the lot
m_i is the mass of the i^{th} particle (g)

Equation F.1 is usually of only theoretical interest because it involves quantities whose values cannot be determined in practice; however, it is the most general formula for the fundamental variance and serves as a starting point for the development of more useful approximation formulas, which are derived using known or assumed properties of the lot.

F.4.2 Scenario 1 – Natural Radioactive Minerals

Gy has derived a practical formula for the fundamental variance based on the following assumptions (Gy, 1992):

- The analyte concentration (actually the critical content) of a particle does not depend on its size. More precisely, if the lot is divided into fractions according to particle size and density, the analyte concentration of each fraction is a function of particle density but not size.

- The distribution of particle sizes is unrelated to density. That is, if the lot is divided into fractions by density, each fraction has approximately the same distribution of particle diameters.

The first of these assumptions is often violated when environmental samples are analyzed for non-natural radionuclides, because in these cases, the analyte concentration of a particle tends to be inversely related to its size The second assumption may also be violated when non-natural materials are involved. However, when natural materials are analyzed for naturally occurring radionuclides, both assumptions may be valid.

Under the two stated assumptions, the fundamental standard deviation σ_{FE} is related to the mass of the lot M_L, the mass of the sample M_S, and the maximum particle diameter d by the equation

$$\sigma_{FE} = k\sqrt{\left(\frac{1}{M_S} - \frac{1}{M_L}\right) d^3} \qquad \text{(F.2)}$$

where k is a constant of proportionality.[6] The "maximum" diameter d is defined as the length of the edge of a square mesh that retains no more than a specified fraction of oversize by mass. Thus, it is *not* the size of the largest particle in the lot. Gy has found it most convenient to let d be the size of a square mesh that retains only 5% oversize, and his definition will be assumed here. According to Gy, this value of d also tends to be the approximate size of the largest particles that are easily identifiable by sight.

When M_S is much smaller than M_L, which is often the case, the fundamental standard deviation is given more simply by

$$\sigma_{FE} = k\sqrt{\frac{d^3}{M_S}} \qquad \text{(F.3)}$$

This formula implies that, to reduce the fundamental standard deviation by half, one may either increase the sample size M_S by a factor of 4 or reduce the maximum particle size d by a factor of $0.5^{2/3} = 0.63$.[7]

F.4.3 Scenario 2 – Hot Particles

As noted, the assumptions of Scenario 1 are often violated when environmental media are analyzed for non-natural radionuclides, because there is usually a correlation between particle size and radionuclide concentration. However, another approximation formula (not due to Gy) may be used if the analyte occurs only in a minuscule fraction of the particles (i.e., "hot particles").

It is assumed that:

- The maximum analyte concentration of a particle z_{max} is known;
- Every particle in the lot has concentration 0 or z_{max} (approximately); and
- The high-activity particles make up a small fraction of the lot both by number and by mass.

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[6]Gy (1992) and Pitard (1993) provide more information about the constant k. MARLAP presents only a brief summary of Scenario 1 because of the difficulty of estimating k.

[7]Equation F.3 also may be understood to say that the fundamental standard deviation is inversely proportional to the square root of the number of particles in the sample.

306 Under these assumptions the fundamental standard deviation σ_{FE} is described by the equation[8]

$$\sigma_{FE} = k\sqrt{\left(\frac{1}{M_S} - \frac{1}{M_L}\right)\frac{z_{max}\delta_H d_H^3}{2z_L}} \qquad \text{(F.4)}$$

307 where

308 M_S is the sample mass (g)

309 M_L is the mass of the lot (g)

310 δ_H is the average density of a high-activity particle (g / cm^3)

311 d_H is the maximum diameter of a high-activity particle, defined as in Scenario 1

312 k is a constant of proportionality.

313 The proportionality constant k depends on the distribution of sizes of the high-activity particles
314 but is most likely to lie between 0.5 and 1.[9]

315 When M_S is much smaller than M_L, Equation F.4 reduces to

$$\sigma_{FE} = k\sqrt{\frac{z_{max}\delta_H d_H^3}{2z_L M_S}} \qquad \text{(F.5)}$$

316 If all the high-activity particles have approximately the same mass and the sample mass is much
317 smaller than the mass of the lot, then Equation F.5 may be rewritten in the simple form

$$\sigma_{FE} \approx \sqrt{\frac{M_L}{M_S n_L}} \qquad \text{(F.6)}$$

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[8]A more complete formula is $\sigma_{FE} = \left[\left(\frac{1}{M_S} - \frac{1}{M_L}\right)\frac{z_{max} - z_L}{2z_{max}}\left(\frac{z_{max} - z_L}{z_L}\delta_H k_H^2 d_H^3 + \delta_G k_G^2 d_G^3\right)\right]^{1/2}$, where δ_G, k_G, and d_G describe the zero-activity particles. Equation F.4 is obtained when z_{max} is much greater than z_L, which happens when the mass of high-activity material is very small.

[9]The constant k equals the square root of Gy's "size distribution factor" g. Gy recommends the value $g = 0.25$ by default for most uncalibrated materials of interest in the mining industry, but no assumption is made here that the same default value is appropriate for hot particles. If all the particles have the same size, $g = 1$.

where n_L is the number of hot particles in the lot. Equation F.6 can also be derived from the fact that the number of hot particles in a small sample can be modeled by a Poisson distribution, whose mean and variance are equal (Chapter 19, *Measurement Statistics*). The fundamental standard deviation equals the coefficient of variation of the Poisson distribution, which is large when the mean is small.

EXAMPLE 1

A 1-kg lot of soil contains approximately 1 Bq/g of ^{240}Pu occurring as hot particles of relatively pure plutonium dioxide ($^{240}PuO_2$, density $\delta_H = 11.4$ g/cm^3, specific activity $z_{max} = 7.44 \times 10^9$ Bq/g) with "maximum" diameter $d_H = 10^{-3}$ cm (10 µm). Assume the distribution of particle sizes is such that $k \approx 0.5$. What is the fundamental standard deviation for a 1-gram sample?

According to Equation F.5,

$$\sigma_{FE} = 0.5\sqrt{\frac{(7.44\times10^{9})(11.4)(10^{-3})^3}{2(1)(1)}} \approx 3.3$$

Thus, the fundamental standard deviation is about 330%, indicating that a 1 g sample probably is inadequate.

If all the hot particles had the same size, then k would equal 1 and the fundamental standard deviation would be about 650%.

When the presence of a small number of hot particles makes it impossible to reduce the fundamental standard deviation to an acceptable value by ordinary means (grinding the material or increasing the sample size), then more innovative methods may be required. For example, the entire lot may be spread into a thin layer and an autoradiograph made to locate the hot particles. Then, if necessary, a biased sample containing essentially all of the hot particles may be taken and analyzed, and the measured result corrected for sample size to obtain the average analyte concentration of the lot.

F.4.4 Scenario 3 – Particle Surface Contamination

A third approximation formula may be used if the contaminant occurs in tiny particles, or even molecules, which adhere *randomly* to the surfaces of larger host particles of the matrix and

cannot be selected without their hosts. In this case, the total mass of the contaminant particles is assumed to be negligible. If the contaminant particles are also extremely numerous, so that many of them adhere to a typical host particle, then the analyte concentration of a particle tends to be inversely proportional to its diameter. In this case the fundamental variance depends primarily on the characteristics of the host particles.[10]

Under the stated assumptions, the fundamental standard deviation σ_{FE} for typical soils is given by

$$\sigma_{FE} = k\sqrt{\left(\frac{1}{M_S} - \frac{1}{M_L}\right)\frac{\delta d^3}{2}} \qquad \text{(F.7)}$$

where

M_S is the sample mass (g)
M_L is the mass of the lot (g)
k is a constant of proportionality
δ is the average particle density (g/cm^3)
d is the "maximum" particle diameter (cm), as defined for Scenario 1

The factor k may vary from lot to lot but is always less than 1 and is usually less than 0.5.

When the sample mass is small, Equation F.7 reduces to

$$\sigma_{FE} = k\sqrt{\frac{\delta d^3}{2M_S}} \qquad \text{(F.8)}$$

The fundamental standard deviation σ_{FE} calculated using Equation F.8 is never greater than $\sqrt{\delta d^3 / 2M_S}$, which is the square root of the ratio of the "maximum" particle mass $\delta d^3 / 2$ to the mass of the sample M_S. *So, as long as the sample is much heavier than the heaviest particle in the lot, the fundamental variance in Scenario 3 tends to be small.* As in Scenario 1, reducing the fundamental standard by half requires either increasing the sample mass M_S by a factor of 4 or reducing the particle diameter by a factor of 0.63. However, note that grinding may cause the

[10]The formula for σ_{FE} given here describes the variability of the total surface area in a sample. A more complete expression includes a term for the variability of the analyte concentration per unit area, but this term is negligible if the number of contaminant particles is sufficiently numerous.

assumptions underlying Equation F.8 to be violated if the contaminant is not redistributed onto the newly created particle surfaces.

EXAMPLE 2

Suppose a 1-kg lot of soil contains ^{90}Sr, which is expected to adhere randomly to the surfaces of the particles. The maximum particle diameter d is found to be approximately 0.2 cm. If nothing more is known about the distribution of particles sizes, what is the maximum fundamental standard deviation for a 1-g sample?

Assuming the density of the soil particles is $\delta = 2.675$ g/cm^3, Equation F.8 with $k = 1$ gives the solution

$$\sigma_{FE} = \sqrt{\frac{(2.675)(0.2)^3}{(2)(1)}} = 0.10 \text{ or } 10\%.$$

Note that since k is usually less than 0.5, the fundamental standard deviation is more likely to be less than 5%.

F.5 Summary

Results derived from particulate sampling theory provide sampling protocols that help to control sampling errors, including sampling bias, fundamental error, and grouping and segregation errors. Some of the important conclusions are listed below.

- For most practical purposes, a sample is guaranteed to be unbiased only if all particles in the lot have the same probability of selection.
- The sample mass should be many times greater than the heaviest particle in the lot, and clumping of particles should be minimized.
- The fundamental variance, which is considered to be the minimum achievable sampling variance, may be reduced by increasing the size of the sample or reducing the particle sizes before sampling.
- Grouping and segregation of particles, which occur because of the particles' differing physical characteristics and the influence of gravity, tend to increase the sampling variance.

- Grouping and segregation errors can be reduced by increment sampling or by splitting. The more increments, the better.

- Correct sampling requires proper tools and procedures.

- Small quantities of particulate material can be homogenized effectively in the laboratory using mechanical mixers that rotate and tumble a closed container, but the effects of mixing tend to be short-lived.

- Estimation of the fundamental variance requires either knowledge or assumptions about the characteristics of the material being analyzed. Quantitative estimates may be crude.

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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	∞

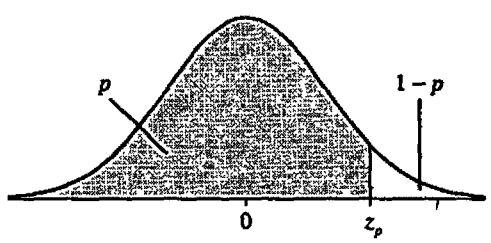
Note: $z_{1-p} = -z_p$

(Continued on next page)

TABLE G.1 (Continued) — Quantiles of the standard normal distribution

(Critical Values)

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	44.99	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

	$\alpha = 0.01$					$\alpha = 0.05$				
	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

	$\alpha = 0.01$					$\alpha = 0.05$				
	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

	$\alpha = 0.01$					$\alpha = 0.05$				
	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

	$\alpha = 0.01$					$\alpha = 0.05$				
	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 — Critical values of Filliben's statistic

n	Significance Level (α) 0.005	0.01	0.025	0.05	n	Significance Level (α) 0.005	0.01	0.025	0.05
					31	0.939	0.948	0.958	0.965
					32	0.939	0.949	0.959	0.966
3	0.867	0.869	0.872	0.879	33	0.940	0.950	0.960	0.967
4	0.813	0.822	0.845	0.868	34	0.941	0.951	0.960	0.967
5	0.803	0.822	0.855	0.879	35	0.943	0.952	0.961	0.968
6	0.818	0.835	0.868	0.890	36	0.945	0.953	0.962	0.968
7	0.828	0.847	0.876	0.899	37	0.947	0.955	0.962	0.969
8	0.841	0.859	0.886	0.905	38	0.948	0.956	0.964	0.970
9	0.851	0.868	0.893	0.912	39	0.949	0.957	0.965	0.971
10	0.860	0.876	0.900	0.917	40	0.949	0.958	0.966	0.972
11	0.868	0.883	0.906	0.922	41	0.950	0.958	0.967	0.973
12	0.875	0.889	0.912	0.926	42	0.951	0.959	0.967	0.973
13	0.882	0.895	0.917	0.931	43	0.953	0.959	0.967	0.973
14	0.888	0.901	0.921	0.934	44	0.954	0.960	0.968	0.974
15	0.894	0.907	0.925	0.937	45	0.955	0.961	0.969	0.974
16	0.899	0.912	0.928	0.940	46	0.956	0.962	0.969	0.974
17	0.903	0.916	0.931	0.942	47	0.956	0.963	0.970	0.975
18	0.907	0.919	0.934	0.945	48	0.957	0.963	0.970	0.975
19	0.909	0.923	0.937	0.947	49	0.957	0.964	0.971	0.977
20	0.912	0.925	0.939	0.950	50	0.959	0.965	0.972	0.978
21	0.914	0.928	0.942	0.952	55	0.962	0.967	0.974	0.980
22	0.918	0.930	0.944	0.954	60	0.965	0.970	0.976	0.981
23	0.922	0.933	0.947	0.955	65	0.967	0.972	0.977	0.982
24	0.926	0.936	0.949	0.957	70	0.969	0.974	0.978	0.983
25	0.928	0.937	0.950	0.958	75	0.971	0.975	0.979	0.984
26	0.930	0.939	0.952	0.959	80	0.973	0.976	0.980	0.985
27	0.932	0.941	0.953	0.960	85	0.974	0.977	0.981	0.985
28	0.934	0.943	0.955	0.962	90	0.976	0.978	0.982	0.985
29	0.937	0.945	0.956	0.962	95	0.977	0.979	0.983	0.986
30	0.938	0.947	0.957	0.964	100	0.979	0.981	0.984	0.987

TABLE G.6 — Summary of probability distributions

Distribution	Parameters	Values	Probability Function	Mode	Mean	Standard Deviation
Binomial	N, p	$k = 0, 1, 2, \ldots, N$	$\binom{N}{k} p^k (1-p)^{N-k}$	$\lfloor Np + p \rfloor$ *	Np	$\sqrt{Np(1-p)}$
Poisson	λ	$k = 0, 1, 2, 3, \ldots$	$\frac{\lambda^k e^{-\lambda}}{k!}$	$\lfloor \lambda \rfloor$ †	λ	$\sqrt{\lambda}$
Rectangular	a_-, a_+	$x \in [a_-, a_+]$	$\frac{1}{a_+ - a_-}$	Not unique	$\frac{a_- + a_+}{2}$	$\frac{a_+ - a_-}{2\sqrt{3}}$
Trapezoidal	a_-, a_+, β $a = \frac{a_+ - a_-}{2}$	$x \in [a_-, a_+]$	$\begin{cases} \frac{x - a_-}{a^2(1-\beta^2)}, & x < \frac{a_- + a_+}{2} - a\beta \\ \frac{1}{a(1+\beta)}, & \left\lvert x - \frac{a_- + a_+}{2} \right\rvert \le a\beta \\ \frac{a_+ - x}{a^2(1-\beta^2)}, & x > \frac{a_- + a_+}{2} + a\beta \end{cases}$	Not unique	$\frac{a_- + a_+}{2}$	$\frac{a_+ - a_-}{2}\sqrt{\frac{1+\beta^2}{6}}$
Normal	μ, σ	$x \in (-\infty, \infty)$	$\frac{1}{\sigma\sqrt{2\pi}} e^{-(x-\mu)^2/2\sigma^2}$	μ	μ	σ
Log-Normal	μ_g, σ_g	$x \in (0, \infty)$	$\frac{\exp(-\ln(x/\mu_g)^2 / 2(\ln\sigma_g)^2)}{x(\ln\sigma_g)\sqrt{2\pi}}$	$\mu_g e^{-(\ln\sigma_g)^2}$	$\mu_g e^{(\ln\sigma_g)^2/2}$	$\mu_g\sqrt{e^{2(\ln\sigma_g)^2} - e^{(\ln\sigma_g)^2}}$
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	0 $(\nu > 1)$	$\sqrt{\frac{\nu}{\nu-2}}$ $(\nu > 2)$
Exponential	λ	$x \in [0, \infty)$	$\lambda e^{-\lambda x}$	0	$\frac{1}{\lambda}$	$\frac{1}{\lambda}$
Chi-Square	ν	$x \in [0, \infty)$	$\frac{x^{\nu/2-1} e^{-x/2}}{2^{\nu/2}\Gamma(\nu/2)}$	$\begin{cases} 0, & \nu \le 2 \\ \nu - 2, & \nu > 2 \end{cases}$	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 $x > 0$.

* If $p = 1$, the mode is N. Otherwise, if $Np + p$ is an integer and $p > 0$, both $Np + p$ and $Np + p - 1$ are modes.

† If λ is a positive integer, both λ and $\lambda - 1$ are modes.

GLOSSARY

The glossary will be prepared following public review

( ) *Indicates the section in which the term is first used in the MARLAP document*