Multi-**A**gency **R**adiological **L**aboratory **A**nalytical **P**rotocols Manual

Volume II: Chapters 10 – 17 and Appendix F

PLANNING

MARLAP

ASSESSMENT   IMPLEMENTATION
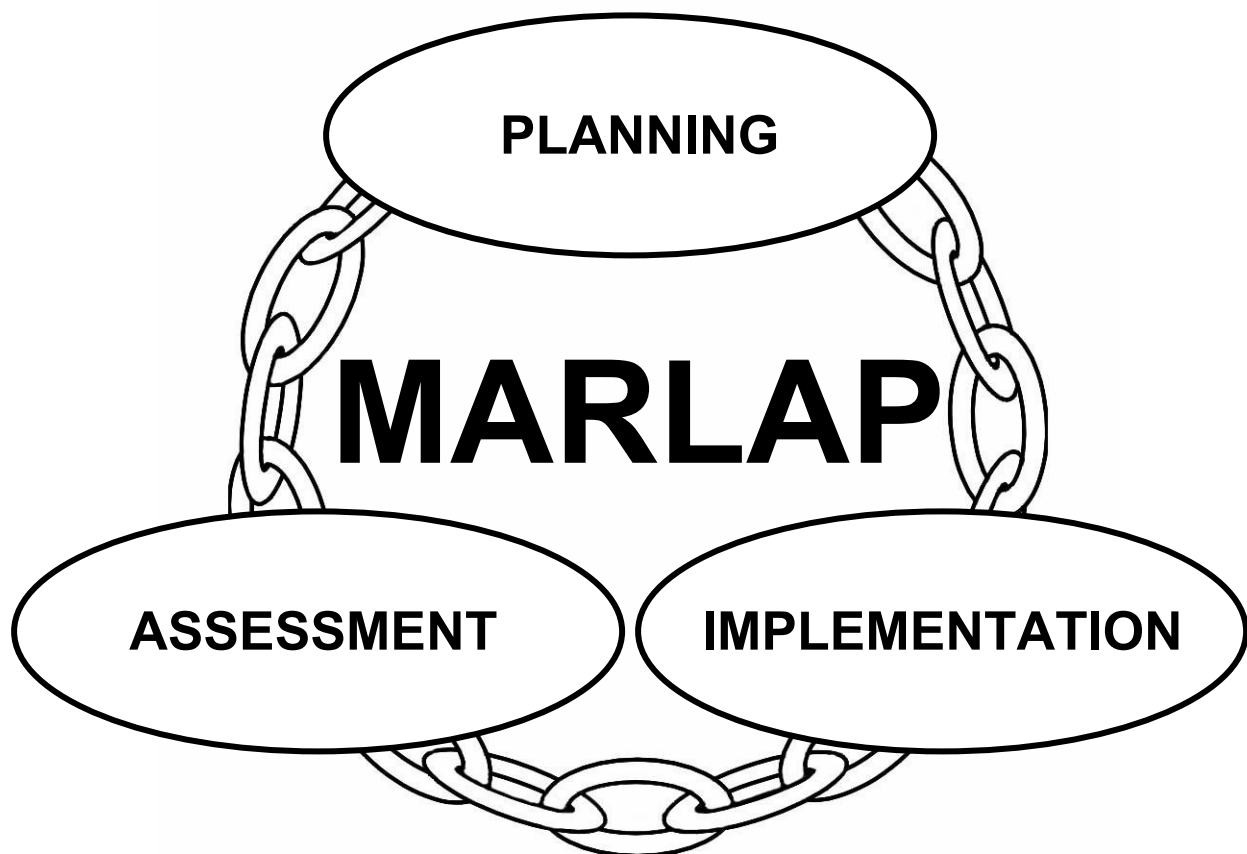
July 2004

Multi-Agency Radiological Laboratory Analytical Protocols Manual (MARLAP)

Part II: Chapters 10 – 17
Appendix F
(Volume II)

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

July 2004

FOREWORD

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

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

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

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

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ACRONYMS AND ABBREVIATIONS

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

OFPP . . . . Office of Federal Procurement Policy

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

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

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

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

$t_{1/2}$ . . . . half-life
TAT . . . . turnaround time
TBP . . . . tributylphosphate
TC . . . . to contain
TCLP . . . . toxicity characteristic leaching procedure
TD . . . . to deliver
TEC . . . . technical evaluation committee
TEDE . . . . total effective dose equivalent
TEC . . . . technical evaluation committee (USGS)
TES . . . . technical evaluation sheet (USGS)
TFM . . . . tetrafluorometoxil™
TIMS . . . . thermal ionization mass spectrometry
TIOA . . . . triisooctylamine
TLD . . . . thermoluminescent dosimeter
TnOA . . . . tri-n-octylamine
TOPO . . . . trioctylphosphinic oxide
TPO . . . . technical project officer
TPP . . . . technical project planning
TPU . . . . total propagated uncertainty
TQM . . . . Total Quality Management
TRUEX . . . . . trans-uranium extraction
TSCA . . . . Toxic Substances Control Act

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

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

V .... volt[s]

WCP .... waste certification plan

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

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

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

UNIT CONVERSION FACTORS

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

10 FIELD AND SAMPLING ISSUES THAT AFFECT LABORATORY MEASUREMENTS

Part A: Generic Issues

10.1 Introduction

This chapter provides guidance to project managers, planners, laboratory personnel, and the radioanalytical specialists tasked with developing a field sampling plan. It emphasizes those activities conducted at the time of sample collection and other activities conducted after sample collection that could affect subsequent laboratory analyses.

A field sampling plan should provide comprehensive guidance for collecting, preparing, preserving, shipping, and 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 (APSs) and the measurement quality objectives (MQOs) that must be met. While comprehensive discussions on actual field sample collection and sampling strategies are beyond the scope of MARLAP, specific aspects of sample collection methods and the physical preparation and preservation of samples warrant further discussion because they impact the analytical process and the data quality.

This chapter has two main parts. Part A identifies general elements of a field sampling plan and provides project planners with general guidance. Part B provides detailed, matrix-specific guidance and technical data 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 to prepare and preserve 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

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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

To design an effective sampling plan, it is critical to obtain the input and recommendations of representatives of (1) the field sampling team, (2) the health physics professional staff, (3) the analytical laboratory, (4) statistical and data analysts, (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 within the field sampling team to ensure that modifications, discrepancies, and changes are addressed and potential problems may be resolved in a timely manner.

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 APSs and statements of work (SOWs), should be consulted, but they cannot address all details. Additional communication will be necessary to convey 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 may include, but are not limited to, 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, custody, and shipment forms;
- Legal accountability, such as chain-of-custody record, when required;
- Selecting samples for field quality control (QC) program;
- Decontaminating equipment and avoiding sample cross-contamination;
- Specifying sample packaging, radiological surveys of samples, shipping, and tracking; and
- Documenting the 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 radiochemical analysis, an important parameter for field personnel is the mass or volume 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 (alpha, beta, and gamma emitters), field logistics, and the radioanalytical methods that are to be employed. It is important to have a quantitative understanding of the relationship between sample size and project specific requirements in order for samples to yield useful data.

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 matrix to be sampled, but also on the accessibility of the matrix and the physical and chemical properties of radionuclide contaminants under investigation.

In addition to specialized field equipment and instrumentation, field sampling supplies commonly include, but are not limited to, 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, and documents;

- Appropriately labeled sample containers;

- Shipment containers and packing materials that meet national and international shipping regulations (see Section 10.2.10);

- Shipment forms;

- Analysis request forms identifying the type of radioanalysis to be performed; and

- Items required by the health and safety plan (medical kit, etc.).

10.2.3 Selection of Sample Containers

There are several physical and chemical characteristics to consider when selecting a suitable container for shipping and storing samples. These 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 be made from 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 or propylene (Teflon™), or polymethylpentene. For certain samples, the choice of containers may require metal construction or be limited to paper envelopes.

10.2.3.2   Container Opening and Closure

A suitable container also should be shaped appropriately for the purpose. For example, a wide-mouthed container will provide easier access for the introduction and withdrawal of sample material and eliminate spills or the need for additional tools or equipment (e.g., funnel) that may become a source of cross contamination among samples.

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

10.2.3.3   Sealing Containers

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

10.2.3.4   Precleaned and Extra Containers

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

10.2.4 Container Label and Sample Identification Code

Each sample can only be identified over the life of a study if a form of permanent identification 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 durable 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 field-sample identification (ID) scheme may introduce bias into the analysis process, such as allowing the laboratory to become aware of trends or locations from the sample identification. This could influence their judgment about the anticipated result and thereby introduce actions on the part of laboratory personnel that they would not otherwise take (such as reanalyzing the sample). 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, or 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 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 standardized preprinted forms are used, all information recorded should be in indelible ink, with all entry errors crossed out with a single line and initialed. The color of ink used should be compatible with the need to copy that information. All entries should be dated and signed on the date of entry. Initials should be legible and traceable, so that it is clear who made the entry.

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

• Identification of Project Plan or Sampling Plan;

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

• Date and time of sample collection;

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

• Suspected radionuclide constituents;

• Sample-specific ID;

• Sample volume, weight, depth;

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

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

• Sample preservation used;

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

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

• Names of field people responsible for collecting sample;

- Physical and meteorological conditions at time of sample collection;

- Special handling or safety precautions;

- Results of field radiation measurements, including surveys of sample containers; 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 forms 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" means an 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. 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 1994). 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 RECORD									
				SAMPLED BY:					
FIELD IDENTIFI-CATION NUMBER	FIELD LOCATION	DATE	TIME	SAMPLE MATRIX			SEQ. No.	No. of Containers	Analysis Required
				Water	Soil	Other			

Relinquished by:	Date/Time /	Received by:	Date/Time /
Relinquished by:	Date/Time /	Received by:	Date/Time /
Relinquished by:	Date/Time /	Received by:	Date/Time /
Relinquished by:	Date/Time /	Received by:	Date/Time /
Relinquished by:	Date/Time /	Received by laboratory for field analysis:	Date/Time /

Method of Shipment:

Distribution: Orig. - Accompany Shipment
1 Copy – Survey Coordinator Field Files

FIGURE 10.1—Example of chain-of-custody record

COC process (APHA, 1998). Guidance is provided in 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 and by project. 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 11.2.4, "Sample Chain-of-Custody," for further information). The COC documents are signed by personnel who collect the samples. A COC 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.

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 QC procedures. QC procedures, therefore, represent specific tools for measuring the degree to which quality assurance objectives are met. Field QC measures are discussed comprehensively in ASTM D5283.

While some types of QC samples are used to assess analytical process, field QC 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 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 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 prepare and package samples properly for transport or shipment by a commercial carrier. All applicable state and federal shipping requirements, discussed later in this section, must be followed. When samples must be shipped by 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 2.5 cm. A minimum thickness of five centimeters should be provided on the container floor.

Samples should also be protected from the potentially adverse impacts of temperature fluctuations. When appropriate, protection from 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 also may serve as the cushioning material.

The requirements for container security, cushioning, and insulation apply regardless of container material. For smaller volume and low-weight samples, properly lined containers constructed from 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, and the lid taped to the can;

- 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 U.S. Department of Transportation regulations, 49 CFR Parts 170 through 189, as well as compliance with the laboratory's license from the U.S. Nuclear Regulatory Commission (NRC; 10 CFR Part 71) and Agreement State (if applicable). International requirements may also apply. See the International Air Transport Association's Dangerous Goods Regulations for additional guidance. These regulations not only set contamination and radiation levels 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 are 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 U.S. Department of Defense, these plans may include imminent threats to life, such as unexploded ordnance, land mines, hostile forces, chemical agents, etc. A few of the hazards particular to field sampling are discussed in the following sections, but these should not be construed as a comprehensive occupational health and safety program. The Occupational Safety and Health Administration's (OSHA) regulations governing laboratory chemical hygiene plans are located at 29 CFR 1910.1450. These requirements should apply as well to field sampling.

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 under-ground 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 trained according to OSHA standards in the proper use of devices to prevent falls.

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, 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 85 dB(A), the eight-hour threshold limit value recommended by the American Conference of Governmental Industrial Hygienists. Exposure to noise levels in excess of 85 dB(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 (1994a–d), 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.

Thermoluminescent dosimeters, film badges, or other personnel dosimeters may be used to monitor and document a worker's external exposures to the whole body or extremities. 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 also may 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 (September 1993);
- NRC Regulatory Guide 8.11, Applications of Bioassay for Uranium (Revision 1, July 1993);
- NRC Regulatory Guide 8.20, Applications of Bioassay for ^{125}I and [131]I (June 1974);
- NRC Regulatory Guide 8.22, Bioassays at Uranium Mills (Revision 1, August 1988);
- NRC Regulatory Guide 8.26, Applications of Bioassay for Fission and Activation Products (September 1980);
- NRC Regulatory Guide 8.32, Criteria for Establishing a Tritium Bioassay Program (July 1988);
- NCRP (1987), Use of Bioassay Procedures for Assessment of Internal Radionuclides Deposition; and
- INPO (1988), Guidelines for Radiological Protection at Nuclear Power Stations.

Part B: 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—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 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 DQOs 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 matrix collected. Sample preservation should 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 samples 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. Sample preservatives may be added to sample collection containers before they are sent to the field.

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 filtered from a liquid or air suspension. 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 typically are classified as aqueous, nonaqueous, or mixtures. Aqueous samples requiring analysis are likely to represent surface water, ground water, drinking water, precipitation, tanks and lagoons, and runoff. Nonaqueous liquids may include a variety of solvents, oils and other organic liquids. Mixtures of liquids represent a combination of aqueous and nonaqueous liquids or a solid suspended in either aqueous and nonaqueous liquids. Standardized water sampling procedures are described in numerous documents (APHA, 1998;

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 can cause some dissolved metals to undergo reaction or precipitation.

Sampling is discussed in NAVSEA (1997) and USACE (1995). The latter reference has been superseded, but the revision does not include sampling. The sampling references listed in USACE (1995) 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 (DOI). 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 Section 3.4.3, "Filters and Wipes." 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 intent is to assess human exposure from ingestion of drinking water "at-the-spigot," 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 involves 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   Example of Guidance for Ground-Water Sample Filtration

After considering whether or not to filter ground-water samples when analyzing for metals, the Environmental Engineering Committee of EPA's Science Advisory Board (EPA, 1997) recommended:

- 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 turbidity units, NTU), then field filtering should not be necessary. For Superfund site assessments, the low-flow sampling technique without filtration is the preferred sampling

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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 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; Puls and Powell, 1992). The literature indicates that colloids as large as 2 µm can be mobile in porous media (Puls and Powell, 1992). 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

The removal of suspended particles is commonly achieved by filtration. When filtration is required, it should be done in the field or as soon as practicable. Field filtration permits acid preservatives to be added soon after collection, which minimizes the adsorption of soluble contaminants on the container walls and avoids the dissolution of particulate matter which may not be part of the sample to be analyzed.

An arbitrary size of 0.45 μm has gained acceptance as the boundary between soluble and insoluble matter (particularly for water in power plant boilers (ASTM D6301). It is the filter pore size that is commonly recommended by laboratory protocols. Material that may be present in colloidal form (a second phase in a liquid that is not in solution), can have particles that range from 0.001 to 2 μm. Such particles may be problematic since they may or may not be filterable (Maron and Lando, 1974). Thus, there can be no single standard for filter type or pore size, and every project should establish its own filtration protocol based upon its needs.

The fact that small particles pass through membrane filters has been recognized for some time (Kennedy et al., 1974). Conversely, as the filters clog, particles an order of magnitude smaller are retained by these filters (Sheldon and Sutcliffe, 1969). 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 type." The screen-type filters (e.g., polycarbonate) clog much more rapidly than the depth type (e.g., cellulose nitrate and acetate) filters. Once the filtration rate drops, particles that would normally pass through the filter are trapped in the material already retained. Also, filtering through screen-type filters may take considerable time and may require suction or pressure to accomplish in a reasonable time. Hence, the use of screen-type filters, because of their increased propensity to clog, generally is 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).

The selected field preservation method also should take into account compatibility with the radionuclides, analytical methods, analytical requirements, and container properties (see Section 10.2.3, "Selection of Sample Containers"). One example that illustrates compatibility with the analytical method is the addition of HCl to water samples as a preservative for gross alpha and gross beta analyses. The HCl will corrode stainless steel planchets used in the method. If laboratory personnel are aware of this, they can include steps to prevent the corrosion. Other preservation issues for liquid samples are discussed in Table 10.1 (page 10-25). Compatibility issues should be evaluated during the planning phase and included in the field sampling plan.

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. Milkey's conclusion is based on: (1) the observation that the loss of uranium, lead, and thorium ions from solution was significantly greater for containers made of polyethylene than of 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 (APHA, 1998, Table 7010.1; EPA, 1980, Method 900.0). Other guidance for sample

preservation by acidification is 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. Adding acid also may cause the generation of CO_2 in the sample, which could purge radon gas.

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

- Acid does not have a direct effect on tritium. However, it may affect the cocktail used in liquid scintillation analysis, or as with HCl, may add significant quench to the cocktail (see Section 15.5.3, "Liquid Scintillation").

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

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

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

PAPER PULP

The addition of paper pulp, with its adsorptive property and large surface area, can avoid the adsorption and loss of easily hydrolyzed radionuclides to the container wall over time (Bernabee et al., 1980). About two grams of finely ground paper pulp are added per liter of acidified sample at time of collection. The pH should be adjusted to one or less and vigorously shaken. The sample may be stored in this condition for an extended period of time. To prepare for analysis, the pulp is removed from solution by filtration and subjected to wet ashing using strong acids (Chapter 12, *Laboratory Sample Preparation*). This ashed solution is commonly added to the original filtrate to make a reconstituted sample solution.

The use of paper pulp and the need for wet ashing, however, pose problems for certain radioanalytical laboratory protocols and must therefore be thoroughly evaluated.

SULFITE

To prevent the loss of radioiodine from solution, sodium bisulfite ($NaHSO_3$), sodium thiosulfate ($Na_2S_2O_3$), or sodium metabisulfite ($Na_2S_2O_5$) may be used. These compounds are strong reducing agents and will convert volatile iodine (I_2) to nonvolatile iodine (I^-). If acid is also employed to preserve samples for analysis of other radionuclides, it is important to note that acid will counteract the effectiveness of the reducing agent. For this reason, samples collected for iodine analyses typically are collected and preserved in a separate container. It should also be noted that the reducing environment produced by the sulfite-type preservatives may convert iron, uranium, and other reducible ions or their compounds to a different oxidation state. The inadvertent change in oxidation state of other radionuclides will have an obvious adverse impact on radioanalytical measurements that require chemical separation. Section 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). 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, such as liquid scintillation cocktails. ^{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.	Causes quench in liquid scintillation cocktails. ^{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.	May produce undesirable oxidation states 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. May crack sample container if frozen too quickly.
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-ray spectrometry 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 nonaerated 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.

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 animals' metabolic discrimination, however, only a few radionuclides have a significant dose impact via the milk pathway, notably ^{90}Sr, ^{131}I, and ^{137}Cs.

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), methimazole (Harrington et al., 1980), 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. Adding formaldehyde to milk samples may require them to be disposed of as hazardous or mixed wastes.

Due to the volatility and potential loss of ^{131}I (as I_2), a known amount of NaI dissolved in water may be added to the milk sample at time of collection if iodine analysis is required. 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 Nonaqueous Liquids and Mixtures

Nonaqueous 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. Nonaqueous 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 nonaqueous liquids and mixtures include waste oils and other lubricants that are generated routinely from maintenance of 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 nonaqueous liquid wastes from routine operations by these facilities, large quantities of nonaqueous 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 by weight 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 tetraacetic acid (EDTA), diethylene triamine pentaacetic 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 be sampled, nevertheless, to assess the amount of residual radioactivity.

The radionuclides that may be encountered with nonaqueous 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), but are not intended to represent a comprehensive list:

- Toluene/xylene/scintillation fluids used by research and clinical institutions: ^{3}H, ^{14}C, $^{32/33}$P, ^{35}S, ^{45}Ca, ^{63}Ni, ^{67}Ga, $^{125/131}$I, ^{99}Tc, ^{90}Sr, ^{111}In, $^{123/125}$I, ^{147}Pm, $^{201/202}$Tl, $^{226/228}$Ra, $^{228/230/232}$Th, $^{232/234/235/238}$U, $^{238/239/241/242}$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, $^{32/33}$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, $^{232/234/235/238}$U, $^{238/239/241}$Pu.

- Other organic solvents from laboratory and industrial operations and cleaning: ^{3}H, $^{32/33}$P, ^{35}S, ^{45}Ca, ^{125}I, U-natural.

- Inorganic and organic acids and bases from extraction processes and decontamination: ^{3}H, ^{14}C, $^{32/33}$P, ^{35}S, ^{54}Mn, ^{67}Ga, $^{125/131}$I, ^{60}Co, ^{137}Cs, and U-natural.

Due to the large number of potential nonaqueous 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 nonaqueous 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 nonaqueous samples are stored for long periods of time, containers should be checked routinely.

10.4 Solids

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

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

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

Unlike liquid samples that may be introduced or removed from a container by simple pouring, solid samples may require a container that is designed for easy sample placement and removal. For this reason, large-mouth plastic containers with screw caps or individual boxes with sealable

plastic liners are commonly used. The containers also minimize the risk for breakage and sample cross-contamination.

10.4.1 Soils

ASTM D653 defines soil as: "Sediments or other unconsolidated accumulations of solid particles produced by the physical and chemical degradation of rocks, and that might or might not contain organic matter." ASTM C999 provides generic guidance for soil sample preparation for the determination of radionuclides. ASTM D4914 and D4943 provide additional information on soil and rock.

The distribution of radionuclides in soil should be assumed to be heterogeneous. The degree of heterogeneity is dictated by the radionuclide's mode of entry into the environment and soil, the chemical characteristics of the radionuclide contaminant, soil composition, meteorological and environmental conditions, and land use. For example, soil contamination from an airborne release of a radionuclide with strong affinity for clay or other mineral constituents of soil likely will exhibit a gradient with rapidly diminishing concentrations as a function of soil depth (the parameter associated with this affinity is K_D, which is the concentration of the solid phase divided by the concentration of the liquid phase). 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 may be insufficient material to complete all the requested analyses (see Section 12.3.1.1 "Exclusion of Material"). 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 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 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 suspected to be present with other nonvolatile contaminants, samples must be split 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 single definition is possible. It is used here to define a laboratory that is close to the point of sample collection. It does not 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.

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. Sediment cores may be sampled, frozen, and then sectioned.

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 10.6) or by scraping, sandblasting, or other abrasive techniques. Volumetric contamination is frequently assessed by nondestructive 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. For most biota, sample preservation usually is achieved by icing samples in the field and refrigeration until receipt by the analytical laboratory. The field sampling plan should describe the type of processing and preservation required.

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.

MEAT, PRODUCE, AND DAIRY PRODUCTS

Samples of meat, poultry, eggs, fresh produce, and other food 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.

ANIMAL FEED AND VEGETATION

Animal feeds also provide important data for determining radionuclide concentrations in the food chain. Crops raised for animal feed and vegetation consumed by grazing farm animals may be sampled. Depending upon radionuclides under investigation and their associated MQOs, kilogram quantities of vegetative matter may be needed.

As in all terrestrial samples, naturally occurring ^{40}K and the uranium and thorium series radionuclides 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.

TERRESTRIAL WILDLIFE

Wild animals that are hunted and eaten may be of interest for potential dose estimates and therefore may require sampling. Examples of wildlife that have been used are deer, rabbits, and rodents that may feed or live in a contaminated site. 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.

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, ^{137}Cs, and the actinides—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

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. Some species of commercial fish, though purchased locally, may have been caught elsewhere. Thus, the presence or absence of a radionuclide in a specific fish may not permit any definite conclusion concerning the presence of the radionuclide in water at that location.

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.

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.

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 and Operation

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 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 calibrated air-flow measuring device with specified accuracy. To calculate the concentrations of any radionuclide in air collected, it is necessary to determine the total volume of air sampled and the associated uncertainties. 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. 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 sample parameters (flow rate, volume, associated uncertainties, 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, nonhygroscopicity, 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 HPS N13.1, 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 Nondestructive 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. Teflon™ fiber filters can be efficient, but they should be used with care because of their high ashing temperatures and difficulties with digestion.

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. Two common methods are to fold filters symmetrically so that the two halves of the collection surface are in contact, or to insert the filter into glassine envelopes. 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.

Since background levels of ^{222}Rn and ^{220}Rn progeny interfere with evaluating alpha air samples, a holdup time of several hours to several days 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 (e.g., $^{131/133}$Xe, ^{85}Kr), ^{14}C as carbon dioxide or methane, ^{3}H as water vapor, gaseous hydrogen, or combined in volatile organic compounds and volatilized radioiodines.

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 HPS N13.1 (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. 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 ⅝ inch (16 mm) diameter by 1½ inch (38 mm) 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 21 hours). Short-period (grab) sampling with charcoal cartridges is possible, with direct counting of the charcoal as soon as possible for gamma emissions.

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 of about 0.11 Bq/L (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 a 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). An alternative method for collecting noble gases by compression into high-pressure canisters is described in Section 15.3.5.1, "Radioactive Gases."

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 (HOT) and as hydrogen gas (HT). However, if tritiated hydrogen (HT) is a suspected component of an air sample (e.g., from a vent or stack), the sampling must take place in the emission point of the gas. This is because the high escape velocity of hydrogen gas causes rapid, isotropic dispersion immediately beyond the discharge point. 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 HOT 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 HOT 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 (HOT) 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 HPS N13.1, Annex H).

A basic system for sampling HOT 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 HOT recovered from the collector is divided by the total volume of air sampled to determine the average HOT-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 HOT 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 HOT from air. HOT 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 HOT 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 HOT. The advantage of using silica gel is that lower HOT-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).

10.5.4.4   Radon Sampling in Air

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 *Health Physics* and *Radiation Research*. Given the voluminous amount of existing information, only a brief overview of the sampling issues that impact laboratory measurements can be presented here.

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. Continuous monitors are not discussed further, since they are less likely to be used by laboratory analysts. Guidance for radon sample collection was published by EPA's Radon Proficiency Program, which was discontinued in October 1998 (EPA 1992; 1993). Additional sampling methods and materials are 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 concentra-tions 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.

The choice among sampling methods depends on whether the measurement is intended as a short-term, quick-screening measurement or as a long-term measurement that determines average exposure or integration. 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 objectives of the investigation. Brief descriptions of several 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 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 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 general terms "flask" or "cell" are used in this discussion. Sometimes they are referred to as "Lucas cells" (Lucas, 1982). The Lucas cell—or alpha scintillation counter—has specific attributes, and not all radon cells are Lucas cells.

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 N13.8) may be used to obtain results in working levels 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 working level 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 working levels.

INTEGRATING SAMPLING DEVICES

By far, the most common technique for measuring radon is by means of integrating devices. Integrating devices, like charcoal canister and the Electret-Passive Environmental Radon Monitor (E-PERM®), 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. Only charcoal canisters are discussed below, since they are more likely to be used by laboratory analysts than electrets and alpha-track detectors.

CHARCOAL CANISTERS

Charcoal canisters 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. The ability of charcoal canisters to concentrate noble gases or other materials may be affected by the presence of moisture, temperature, or other gaseous or particulate materials that may foul the adsorption surface of the charcoal.

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, "Wipe Samples"). 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." Frame and Abelquist (1999) provide a comprehensive history of using smears for assessing removable contamination.

The purpose of the wipe test, organizational requirements or regulations, the nature of the contamination, the surface characteristics, and the radionuclide all influence the conditions for the actual wipe-test process. The wipe-test process should be standardized to ensure that the sampling process is consistent. Since surfaces and wipe materials vary considerably, wipe-test results provide qualitative indication of removable contamination. Fixed contamination will, by definition, not be removed. Therefore, direct measurements may be necessary to determine the extent on contamination.

The U.S. Nuclear Regulatory Commission (NRC, 1981) suggests that 100 cm² 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).

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 either should dissolve in the cocktail or become transparent to the counting system.

10.6.1 Sample Collection Methods

10.6.1.1 Dry Wipes

Dry wipes (smears) for removable surface activity usually are obtained by wiping an area of 100 cm^2 using a dry filter paper of medium hardness while applying moderate pressure. A 47 mm diameter filter typically is used. This filter can be placed into a proportional counter for direct counting. Smaller filters may be advantageous when the wipe is to be counted using liquid scintillation counter for low energy beta-emitting radionuclides, such as tritium, ^{14}C, and ^{63}Ni. The choice of wipe-test media and cocktail is critical when counting low-energy beta-emitting radionuclides in liquid scintillation counters, because the liquid scintillation counting process depends on the detection of light produced by the interaction of the radiation with the cocktail. The filter may absorb energy from the radiation (see "Quench" under Section 15.5.3.3). A filter that is in the cocktail can prevent light from being seen by both detectors at the same time. If light is produced and seen by only one of the two detectors typical in liquid scintillation counting systems, then the count will be rejected as noise. A filter/cocktail combination that produces a sample that is transparent to the counting system is the best combination for liquid scintillation counting. Background produced by the filter may also be a consideration.

For surveys of small penetrations, such as cracks or anchor-bolt holes, cotton swabs are used to wipe the area of concern. The choice of material for wipe-testing for special applications is critical (Hogue, 2002), and the material selected can significantly affect the efficiency of the removal of surface radioactivity. Usually, switching wipe test material should be avoided during a project, when possible. Samples (dry wipes or swabs) are placed into envelopes or other individual containers to prevent cross-contamination while awaiting analysis. Dry wipes 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 dry wipes 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.

Additional information on wipe-test counting can be found in ISO (7503-1; 7503-2; 7503-3), which apply to surfaces of equipment and facilities, containers of radioactive materials, and sealed sources. Abelquist (1998) discusses using smears to assess the quantity of removable contamination as it applies to radiological surveys in support of decommissioning, compliance with DOT shipping criteria, and operational radiological protection programs.

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 (Campbell 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 that 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. Recovery from absorbent surfaces, such as laboratory bench paper or untreated wood, also may be poor 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 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 laboratory, 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.

10.6.3 Analytical Considerations for Wipe Material Selection

Some analytical considerations for selecting wipe materials are included here, because field sample collection and subsequent sample counting usually occur without such intervening steps as sample preparation, sample dissolution, or separation. It is critical, therefore, to ensure that the wipe material used for collection and the actual counting process are compatible. The following paragraphs offer some general guidance for proportional and liquid scintillation counting. The final paragraph discusses some key issues that impact dissolution of wipes.

The wipe should remain flat during counting in order to maintain optimum counting geometry in an automatic proportional counter. Wipe material that can curl may jam an automatic counter and destroy the detector window of the counter, become a source of cross-contamination of samples, or contaminate the counting system. Most proportional counting systems use two-inch (5 cm) planchets, and the wipe should fit into the planchet. If not, a subsample will need to be taken, and subsampling adds additional uncertainty due to sample homogeneity considerations.

When wipes are put directly into a liquid scintillation cocktail, the wipe should not add color or react with the cocktail. For maximum counting efficiency and reproducibility, the wipe either should dissolve or become transparent to the counting system. When wipes that have an adhesive backing are put directly in a liquid scintillation cocktail, the adhesive may not dissolve completely. Compatibility should be checked before use to prevent problems during actual sample analysis. Special cocktails are available to dissolve filters, but they may cause a waste-disposal problem. Since the possible combination of cocktails and filters is large, only general guidance is provided here. Consult the manufacturer's specifications for specific guidance.

When it is necessary to do destructive analysis on a wipe, select a wipe that can be destroyed easily or dissolved during the sample preparation steps, and the residue will not cause interference problems in the subsequent counting. Some wipes have adhesive backing; the wipe materials may dissolve easily but the adhesive backing may not. Additional steps would then be necessary to destroy the adhesive backing. Dissolving glass-fiber wipes may require the use of hydrofluoric acid. These extra processes can add time or cost to the analysis. See Section 10.5.2 ("Filter Selection Based on Destructive Versus Nondestructive Analysis"), Section 12.5 ("Wipe Samples") and Chapter 13 (*Sample Dissolution*) for additional information.

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11 SAMPLE RECEIPT, INSPECTION, AND TRACKING

11.1 Introduction

This chapter provides guidance on laboratory sample receiving and surveying, inspecting, documenting custody, and assigning laboratory tracking identifiers (IDs). These topics are presented sequentially in this chapter, but they may be performed 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. Within MARLAP, the "sample receipt" process includes the surveying of the package and sample containers for radiological contamination and radiation levels. "Sample inspection" means checking the physical integrity of the package and samples, confirming the identity of the sample, confirming field preservation (if necessary), and recording and communicating the presence of hazardous materials. "Laboratory sample tracking" is a process starting with logging in the sample and assigning a unique laboratory tracking identifier (numbers and/or letters) 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 (see Section 10.2, "Field Sampling Plan: Non-Matrix-Specific Issues").

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 (Figure 11.1). 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. Effective communications 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 radioactive materials license conditions and proper operating procedures, are also discussed because these topics are linked to receipt, inspection, and tracking activities. The 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 on radiological issues can be found in NRC (1998a; 1998b).

11.2 General Considerations

11.2.1 Communication Before Sample Receipt

Before the samples are received, the laboratory should know the approximate number of samples that will be received within a specific

Contents

Field Sample Shipment (see Chapter 10)
Tracking Documents
• Number and type of samples along with field sample number
• Field processing and preservation
• Analysis requested

Sample Receipt

Sample received in designated area
• Authorized user notified for radiological screening of package
• Check for evidence of breakage or leakage of exterior of shipping package, then shipping containers. If found, radiologically survey and decontaminate if necessary
• Radiological survey
• License requirements
• Chain-of-custody procedures if required

Laboratory Tracking

Sample Inspection

In designated rad receiving/prep area:
• Check container labels against sample
• Check radionuclides requested against tracking documents
• Check tamper seals
• Verify preservation against tracking documents
• Check field preparation against tracking documents

Any discrepancies in the following will result in corrective action:
• Survey limits
• Expected radionuclides
• Number and type of samples
• Tracking Documents

SAMPLE REJECTED

SAMPLE ACCEPTED

Check with client relative to sample disposition

Short-term sample storage or sample prep/analysis laboratory

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

period of time 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). The information about the client, points of contact, number of samples, and types of analyses can be entered into the laboratory information management system (LIMS) to facilitate communication between the laboratory—in both the sample receipt area and the project management area—and the project manager. 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 any 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 storage space 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 use its LIMS to generate labels and bar-codes for the appropriate containers to be used in the field. This process would assist in assigning appropriate sample IDs for the laboratory tracking system, which starts with sample receipt. The laboratory should instruct the field staff to place the tracking documents on the inside of the cooler lid for easy access and to include any other pertinent information (field documentation, field surveying information, etc.).

11.2.2 Standard Operating Procedures

A laboratory should have standard operating procedures (SOPs) for 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 • Surveying methods
Inspection:	• Check physical integrity • Confirm sample identification • Identify/manage hazardous materials • pH measurement instructions • Use the laboratory information management system (LIMS) to assign laboratory sample IDs
Tracking:	• Maintain chain of custody and document sample handling during transfer from the field to the laboratory, then within the laboratory • Ensure proper identification of samples throughout process • Procedures to quickly determine location and status of samples within 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 laboratory

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

Laboratories that handle radioactive materials are required (with few exceptions, such as certain U.S. Department of Energy National Laboratories and Department of Defense laboratories) 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 client must have a copy of the current radioactive materials license for the facility to which the samples are being shipped. The laboratory staff and the project manager all 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 information 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.

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 Section 10.2.7). 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 states 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 (see Figure 10.1). 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 surveyed for external surface radiological contamination and radiation level, 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 surveying). 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 surveying and observation of its physical integrity).

11.3.1 Package Receipt

Some laboratories require arriving samples to go through a security inspection process at a central receiving area before routing them to the appropriate laboratory area(s). In addition, if samples are shipped by an air transport carrier, the shipping containers may be subject to airport security. In these cases, the container housing the samples may be opened and the samples inspected and reinserted in an order not consistent with the original packaging. In these cases, it is imperative that each individual sample container have a permanent identifier either in indelible ink or as a label affixed on the side of the sample container (see Section 10.2.4, "Container Label and Sample Identification Code"). Within each shipping container, a separate sample packing slip or tracking documents that lists the samples (by sample ID) for the container should be included.

Packages should be accepted only at designated receiving areas. 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 tracking documents 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.

Surveying 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 survey 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 its 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. The project manager should be contacted about possible disposition of any samples.

11.3.2 Radiological Surveying

In addition to ensuring compliance with the laboratory's license and verifying estimates of radio-nuclide activity (Section 11.3.1), the radiological surveying 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 surveyed for external contamination using a wipe (sometimes referred to as a "swipe") and for surface exposure rate using the appropriate radiation survey meter. Exceptions may include known materials intended for analysis as: well-characterized samples, bioassays, or radon and associated decay products in charcoal media (exceptions should be listed in the laboratory SOP). Surveying 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 surveyed 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 surveyed individually. These procedures should include the action level and appropriate action as established by the facility. Personnel performing surveying procedures should be proficient in the use of portable radiation surveying 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 surveying 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 surveying 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 surveying must be performed no later than three hours from the beginning of the next workday.

Survey 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 (swiped). Wipes are not always used, but if there is reason to believe that something has leaked, then wipes should be used. This survey 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, such a survey can help to avoid introducing a high-activity sample into a low-activity area. 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 [of NRC, 1998b].

- 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 them 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.

In addition to these, laboratories may have additional internal notifications or procedures.

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 surveying, tracking, and handling or processing of critical short-lived radionuclides.

11.4.1 Physical Integrity of Package 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.

Sample containers that have leaked (from a loose lid or puncture) may still hold enough sample for the requested analyses, so the laboratory should first determine whether sufficient representative sample remains. The sample is not usually analyzed if its integrity was compromised or is in doubt. 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.

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 tracking documents 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 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 nonconformance. Visual inspection can be used to:

• Verify identity of samples by matching container label IDs and tracking documents;

• Verify that the samples are as described by matrix and quantity;

• Check the tamper seal (if used);

• Verify field preparation (e.g., filtering, removing extraneous material), if indicated; and

• Note any changes to samples' physical characteristics that are different than those in the tracking documents.

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. 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 surveying for chemical contaminants using surveying 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 (e.g., 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's chemical hygiene officer and the project manager should be notified 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 (e.g., there is no corresponding filter or there are obviously solid particles in a 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 or 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. 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 sample ID 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 receipt 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 IDs should be assigned to each sample in accordance with the laboratory's SOP on sample codes. Each sample should receive a unique sample ID by which it can be logged into the LIMS, scheduled for analysis, tracked, and disposed. Information to be recorded during sample log-in should include the field sample identification number, laboratory sample ID, 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 analysis (e.g., analytical requirements or MQOs) and tracking of samples at the laboratory. Laboratory sample tracking is a continuation of field sample tracking. Some of this information may have been entered into the LIMS during the planning phase.

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 surveying, along with the assigned tracking identification, passes to

the laboratory where specific preparation and analyses are performed. The sample may be further subsampled. Each subsample, along with the original sample, requires tracking to account for all materials handled and processed in the laboratory.

Each set of samples received by the laboratory should be accompanied by documents identifying the analytes required for each sample. These documents should be reviewed against the project plan documents or the SOW, which should identify the analytes, matrices, and analytical requirements and be part of the project documentation prior to the samples being received by the laboratory. 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 laboratory sample ID).

Aliquants used during the analytical process can be tracked using analysis laboratory notebooks, forms, or bench sheets that record laboratory sample IDs, 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 and are used to assist in sample tracking. Each sheet is helpful for identifying and processing samples in batches that include designated QC 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 IDs, 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 should be placed in a secure area. 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 should 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 should 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 should be made with the authorized user. See Chapter 17 for more information on waste disposal.

11.6 References

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12 LABORATORY SAMPLE PREPARATION

12.1 Introduction

On first impression, sample preparation may seem the most routine aspect of an analytical protocol. However, it is critical that analysts realize and remember that a measurement 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.

(After Scwedt, 1997)
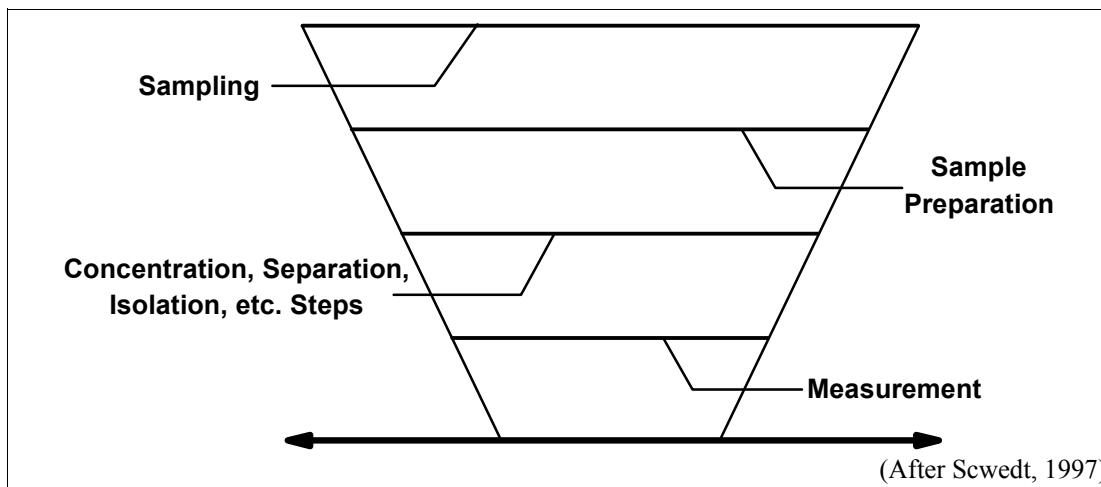
FIGURE 12.1—Degree of error in laboratory sample preparation relative to other activities

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

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for sample preparation to avoid sample loss and sample contamination. Due to the physical nature of the matrix, 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, 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 (Section 14.9) 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 air flow 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 to increase the surface area and speed up the reaction between the sample and the fluxing agent or

acid (see Chapters 13 and 14 on dissolution and separation). 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 due 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 properly constructed sealed vessel. 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 depending upon 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 due 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. Analysis for tritium in soils should avoid these types of sample preparation prior to analysis. Instead, total water content should be determined separately. Tritium analysis then could be performed by adding tritium-free ("dead") water to an original sample aliquant followed by filtration or distillation.

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°
	Magnesium, calcium, and sodium carbonates	Natural ores of these metals decompose between 825° and 1,330° to yield the respective metal oxides
Iodine — ^{131}I, ^{129}I	I_2	185.2° (sublimes readily)
Cesium — ^{134}Cs, ^{135}Cs, ^{136}Cs, ^{137}Cs	Cs^0 (as metal) Cs_2O (as metallic oxide) (nitrates decompose to oxides) CsCl (as metallic chloride)	678.4° (melts at 28) ~400° 1290°
Technetium — ^{99}Tc	Tc_2O_7 $TcCl_4$ TcO_2 [Most Tc compounds sublime above 300°. Tc(VII) is an oxidant that reacts with organic solvents forming Tc(IV)]	310.6° Sublimes above 300° Sublimes above 900°
Polonium — ^{208}Po, ^{209}Po, ^{210}Po	Po^0 $PoCl_4$ $Po(NO_3)_4$ [as a solid] PoO_2	962° 390° Decomposes to PoO_2 above ~150° Decomposes to Po metal above 500°
Lead — ^{210}Pb, ^{212}Pb, ^{205}Pb	Pb^0 $PbCl_2$ $Pb(NO_3)_2$ PbO	1744° 950° Decomposes to oxide above 470° 888°

* The closer the sample preparation temperature is to the boiling point of the compound, the more significant will be the loss of the material. However, if the objective is to distill the analyte compound from other nonvolatile materials, then boiling temperature is needed. Sample preparation near the decomposition temperature should be avoided for those compounds that have a decomposition temperature listed in the table.
Sources: Greenwood and Earnshaw (1984); Windholz (1976); Schwochau (2000); Sneed and Brasted (1958).

Additional elements that volatilize under specific conditions include arsenic, antimony, tin, polonium, lead, selenium, mercury, germanium, and boron. Chromium can be volatilized in oxidizing chloride media. Carbon, phosphorus, and silicon may be volatilized as hydrides, and chromium is volatilized under oxidizing conditions in the presence of chloride. The elements in Table 12.1 are susceptible to changing oxidation states during sample preparation. Thus, the pretreatment should be suited to the analyte. The volatility of radionuclides of tritium, carbon, phosphorus, and sulfur contained in organic or bio-molecules is based on the chemical properties of those compounds. If such compounds are present, special precautions will be necessary during sample preparation to avoid the formation of volatile compounds or to capture the volatilized materials.

12.2.1.3   Losses Due to Reactions Between Sample and Container

Specific elements may be lost from sample materials from 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 due 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 that form alloys with platinum. Porcelain should 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, minimizing the loss of the sample's trace materials to the container surface.

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 1,100 °C); fragile; more expensive than glass; attacked by HF, H_3PO_4, and alkaline solutions.
Porcelain	High temperature applications and pyrosulfate fusion	Used at temperatures up to 1,100 °C; less expensive than quartz; attacked by HF, H_3PO_4, and alkaline solutions.
Nickel	Molten alkali metal hydroxide and Na_2O_2 fusions	Suitable for use with strongly alkaline solutions. Do not use with HCl.
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.
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. Do not use with KF or HF.

Material	Recommended Use	Properties
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 below 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).
Polystyrene	Sample and reagent storage	Only useful for acid solutions < 0.1 M; brittle

The internal surface area of a container, whether used for sample preparation or storage, may cause loss of analyte. Scratches and abrasions increase the surface area, and their geometry make loss of analyte likely. Thus, it is important to discard containers that are scratched or abraded on their interior surfaces.

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 14);
- Glassware/equipment;
- Facilities; and
- Cross-contamination between high- and low-activity samples.

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 μm) 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, volatile radionuclides (including tritium), 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 grinding or pulverizing of solid samples or the handling of samples that could produce airborne contamination should be carried out under a laboratory hood or ventilated enclosure designed to prevent dispersal or deposition in the laboratory of contaminated air particulates. These particles easily can contaminate other samples stored in the area. To prevent such cross-contamination, other samples should be covered or removed from the area while potential sources of airborne contamination are being processed.

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

12.2.2.2 Contamination of Reagents

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

12.2.2.3   Contamination of Glassware and Equipment

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

Whenever possible, the use of new or disposable containers or labware is recommended. For example, disposable weigh boats can be used to prevent contamination of a balance. Disposable 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. Such a program should address possible samples of varying activity or characteristics. This minimizes sample cross-contamination through laboratory processing equipment (e.g. filtering devices, glassware, ovens, etc).

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, HNO₃, or citric acid), and a rinse with deionized or distilled water. As noted in Chapter 10, scrubbing glassware with a brush aids in removing contaminants.

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 due 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, which is the formation and collapse of submicron bubbles. These bubbles form and collapse about 25,000 times each second with a violent microscopic intensity that 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.

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 (by volume) 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. Additional cleaning of 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. (2001). 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 washing).

- 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 (Section 12.3.1.4 and Appendix F, *Laboratory Subsampling*). 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.

12.3.1 General Procedures

The following sections discuss the general procedures for exclusion of material, heating solid samples (drying, charring, and ashing), obtaining a constant weight, mechanical manipulation grinding, sieving, and mixing), and subsampling. Not every step is done for all solid sample categories (soil/sediment, biota, and other) but are presented here to illustrate the steps that could be taken during preparation.
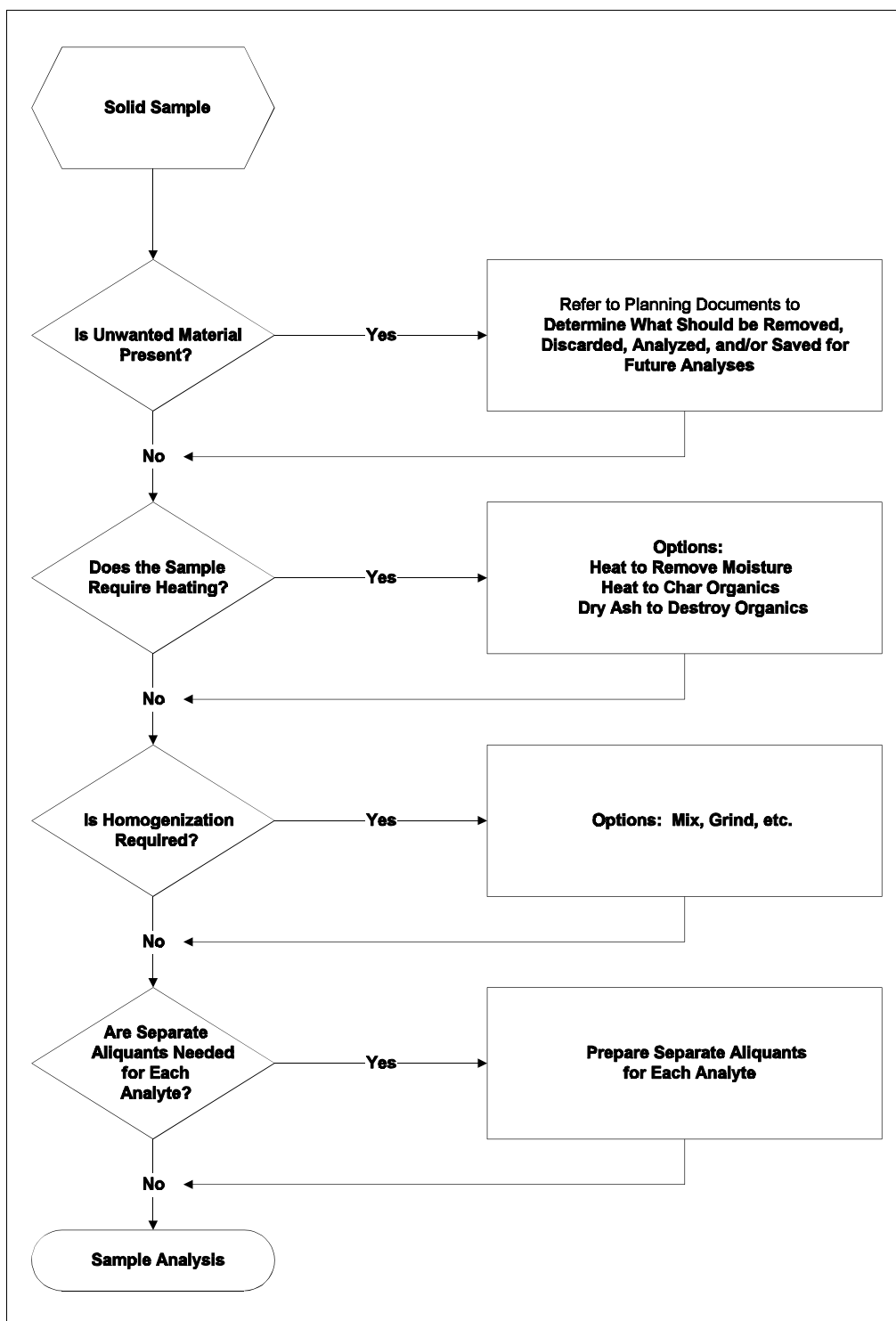
FIGURE 12.2—Laboratory sample preparation flowchart (for solid samples)

12.3.1.1   Exclusion of Material

EXCLUSION OF MATERIAL BY SIZE AND COMPOSITION

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

EXCLUSION OF ORGANIC MATERIAL

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

12.3.1.2   Principles of Heating Techniques for Sample Pretreatment

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

- To remove moisture or evaporate liquids, raise the temperatures to 60 to 110 °C, which will not significantly alter the physical composition of the sample.

- To prepare a sample containing organic material for subsequent wet ashing or fusion, "char" the material by heating to medium temperature of 300 to 350 °C (see page 12-19 on "Charring of Samples").

- To prepare the sample for subsequent determination of nonvolatile constituents, dry ash at high temperature of 450 to 750 °C. This may significantly change the physical and chemical properties of the sample.

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 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.

- Adsorbed 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 usually can 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 Official 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 solid standards from the National Institute of Standards and Technology (coal, clays, limestone, sediment) and foods and food materials (rice and wheat flour), and Koh (1980) who discusses microwave drying of biological materials.

Container Material. A sample container's 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. Polyethylene 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. The release of vacuum should be accomplished by the slow introduction of dry or ambient-humidity air into the chamber.

(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 that 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, and 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 (300 to 350 °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. Most organic compounds will char and decompose in the range of 300 to 350 °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) that 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 that 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 that 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.

Time. The duration required to completely combust a sample depends on the size of the sample, the chemical and physical form of the sample before and after ashing, and the maximum temperature required to ash the sample. In many cases, it is convenient to place the sample in an unheated furnace and gradually raise the temperature during the day until the maximum temperature is achieved. The furnace is then left at the maximum temperature overnight (12 hours). The furnace is allowed to cool during the next day, and samples are removed from a cold oven. This procedure helps prevent sudden changes in temperature that could cause air currents that may potentially disturb the ash. An alternative is to leave the sample at maximum temperature for 24 hours and let the sample cool in the oven the second night to ensure complete combustion of the sample.

The elapsed time for dry ashing samples can be significant (greater than 36 hours), but the actual time required by laboratory personnel is minimal.

TABLE 12.3 — **Examples of dry-ashing temperatures (platinum container)**

Element	Temperature/Matrix
Cobalt	450–600 °C for biological material; some losses reported due to reactions with crucible; increased volume of sample increases volume of ash and limits loss of sample.
Cesium	400–450 °C for food and biological material; CsCl and $CsNO_3$ begin to volatilize when held at temperatures above 500 °C for any length of time.
Iodine	450–500 °C with an alkaline ashing aid to prevent volatilization; losses reported for temperatures as low as 450 °C even with alkaline ashing aids added; total volatilization >600 °C.
Lead	450–500 °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	450–550 °C for plants, 600 °C for meat, 700 °C for milk and bone.
Technetium	725–750 °C for plants treated with ammonia.
Thorium	750 °C for bone.
Uranium	600 °C for coal, 750 °C for biological material; uranium reacts with porcelain glaze resulting in sample losses.

Source: Bock (1979).
(Note that reducing conditions for platinum containers are given in Table 12.2)

12.3.1.3 Obtaining a Constant Weight

If required, constant weight is obtained by subjecting a sample to repetitive cycles of drying and weighing until a series of weights meets specified requirements. Project-specific planning documents or laboratory SOPs should define the acceptance criteria. For example, in Greenberg et al. (1992), solids are repetitively heated for an hour, then weighed until successive weighings agree within 4 percent of the mass or within 0.5 mg. In the ASTM guidelines for the preparation of biological samples (ASTM D4638), an accurately weighed sample (1 to 2 g ± 0.1 mg, 5 to 10 g ± 1 mg, >10 g ± 10 mg) is heated for 2 hours, cooled in a desiccator, and weighed. Drying is repeated at hourly intervals to attain a constant weight within the same accuracy. The consistent drying of materials from a large sample set may require a qualitative evaluation of change in the sample composition. If a qualitative change occurs the drying method may need to be checked for completeness. One way to do this would be to perform routine dry-to-constant-weight evaluations on separate samples.

Laboratory conditions and handling of the samples by the analyst during sample weight determinations can increase the uncertainty of the final sample mass.

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 that 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, *Laboratory Subsampling*).

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

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

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

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

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

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

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

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

When dealing with solid samples, it is often necessary to grind the sample to reduce the particle size in order to ensure homogeneity and to facilitate attack by reagents. Obenauf et al. (2001) is an excellent resource for information regarding grinding and blending.

For hand grinding, boron carbide mortars and pestles are recommended. For samples that can be pulverized by impact at room temperature, a shatterbox, a mixer-mill, or a Wig-L-Bug™ is appropriate, depending on the sample size. For brittle materials—such as wool, paper, dried plants, wood, and soft rocks—which require shearing as well as impact, a hammer-cutter mill is

warranted. For flexible or heat-sensitive samples such as polymers, cereal grains, and biological materials, cryogenic grinding is necessary. Methods are described below:

• A shatterbox spins the sample, a puck, and a ring inside a dish-shaped grinding container in a tight, high-speed horizontal circle. Within two to five minutes, approximately 100 grams of brittle material can be reduced to less than 200 mesh. Shatterboxes are used typically 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 example of a laboratory mill for pulverizing and blending very small samples, typically in the range of 0.1 to 1 mL.

• A hammer-cutter mill uses 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 used. 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 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.

The analysis of solid samples from the environment contaminated with radioactivity represents a special challenge. In most cases, the radioactive materials will be from different sources than the solid sample. Thus the contamination of solid samples with anthropogenic sources of radionuclides will result in a non-uniform particle mix as well as a non-uniform size distribution. This further emphasizes the need for unbiased subsampling procedures.

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 C999 provides guidance on 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) describe 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 (6.25 mm) 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. It 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

ASTM D4638 is a standard guide for the preparation of biological samples for inorganic chemical analysis. It 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.

12.3.3.1   Food

The International Atomic Energy Agency offers a guidebook for the measurement of radionuc-lides in food and the environment, which includes guidance on sample preparation (IAEA, 1989). Additionally, methods are presented in HASL-300 (DOE, 1997) for the preparation of milk, vegetables, composite diets, etc. (Table 12.4). These methods involve dry ashing samples containing non-volatile radionuclides. Initially the samples are completely dried at 125 °C, and then the temperature is raised slowly over an eight-hour period to 500 °C. As the samples are heated, they will reach ignition temperature. It is important to pass through this ignition temperature range slowly without sample ignition. With careful adjustment of the ashing temperature in a stepwise fashion over this eight-hour interval, sample ignition can be avoided. Table 12.4 lists the ignition temperature ranges for various foods. Once through the ignition temperature range, the temperature can be raised more rapidly to 500 °C. The samples can then be ashed at 500 °C for 16 hours. Ignition sometimes cannot be avoided if the sample type contains large amounts of fat. In addition, glowing of carbonaceous material due to oxidation of carbon will be evident during the ashing process. If only a portion of ash is to be used for analysis, it is ground and sieved prior to aliquanting.

TABLE 12.4 — Preliminary ashing temperature for food samples (Method Sr-02-RC, HASL-300 [DOE, 1997])	
Material	**Temp (°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

12.3.3.2   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 (DOE, 1997) also describes sample preparation techniques for vegetation samples for a variety of radionuclides.

12.3.3.3   Bone and Tissue

Bone and tissue samples can be dry ashed in a muffle furnace (DOE, 1997; 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 that 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 Section 10.3.2, "Filtration").

Filter samples from liquids usually consist of the filter with the associated solid material. For samples with a large amount of sediment, the solid material may be removed from the filter and analyzed as a solid. When there is a relatively small amount of solid material, the filter may be considered as part of the sample for analytical purposes. When large volumes of liquid are processed at high flow rates, filter cartridges often are used. Typically, the cartridge case is not considered part of the sample, and laboratory sample preparation includes removing the filter

material and sample from the cartridge case. Any special handling instructions should be included as SOPs in the planning documents.

Air filters may be particulate filters, which are prepared in the same manner as liquid filters, or they may be cartridges of absorbent material. Filters that absorb materials are typically designed for a specific analysis. For example, activated charcoal cartridges are often used to collect samples of iodine or radon. Silver zeolite cartridges generally are used for sampling iodine isotopes. These cartridges are often designed to be analyzed intact, so no special sample preparation is needed. If the cartridges need to be disassembled for analysis, a special SOP for preparing these samples is usually required.

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

12.5 Wipe Samples

Wipe samples (also referred to as "swipes" or "smears") are collected to indicate the presence of removable surface contamination. The removable contamination is transferred from the surface to the wipe material. The type of filter (paper, membrane, glass fiber, adhesive backing, etc.) and counting method influence the preparation requirements (Section 10.6, "Wipe Sampling for Assessing Surface Contamination").

Wipes are usually counted directly without additional sample preparation. Wipe samples can be counted directly with a gas flow proportional counter for alpha or beta radioactivity. For gamma-emitting radionuclides, the wipe also can be counted directly. For very low-energy emissions, wipe samples are commonly counted by liquid scintillation (see Chapter 15, *Quantification of Radionuclides*).

When destructive analysis is required, the techniques in Chapter 13, *Sample Dissolution*, and Chapter 14 *Separation Techniques*, should be followed. Some wipes have adhesive backing that can complicate digestion and require more aggressive treatment with acid to dissolve. When counting with liquid scintillation, the compatibility of the processed wipe with the cocktail is an important consideration.

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. In many cases, the results of preliminary measurements can be used to determine the quantity of sample to be used for a specific analysis.

These preliminary measurements typically require little or no sample preparation. However, they should be performed on a separate portion of the sample. This avoids any unexpected degradation of the sample parameters during transport and storage, and allows laboratory analysts to focus on radiochemical analyses. Using a separate aliquant also helps to prevent cross-contamination of samples sent to the laboratory or loss of radionuclides through interaction with field-measuring equipment.

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. Project planning documents should specify the acceptable turbidity limit for of aqueous samples for direct sample processing without removing solids.

12.6.3 Filtration

The filtration of samples is based on the appropriate plan document that 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 10.3.2. However, preservatives should not be added until sample filtration has been performed (if stipulated in the project DQOs). This ensures that insoluble materials in the sample that might be entrained during sample collection do not affect the analytical results.

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). PNL/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 adding 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 radiochemical preparation techniques for freshwater and seawater samples are illustrated in 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 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 non-aqueous 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 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

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[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 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 1g/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.

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 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 (1989) may be used to demonstrate 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, including Cehn (1979), Eichling (1983), Allied Chemical (1982), and 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) or with nitric acid and peroxide (RESL, 1982). Alternatively, there are procedures that 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 (DOE, 1997), or prepared by lyophilization, "freeze drying" (Dugan and McKibbin, 1993).

It is important to note that although ANSI N13.30 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.

12.9 References

12.9.1 Cited Sources

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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 Chapter 14 (*Separation Techniques*), but their importance to dissolution is reviewed here.

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 measurement 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 or mineral acids to produce a homogeneous aqueous solution, 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.

The choice of technique is determined by the type of sample and knowledge of its physical and chemical characteristics. Fusion and wet ashing techniques may be used singly or in combination to decompose most samples analyzed in radioanalytical laboratories.

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Leaching techniques are used to determine the soluble fraction of the radionuclide of interest under those specific leaching conditions. Different formulas for leaching agents will yield different amounts of leachable analyte. It should be recognized that the information so obtained leaves unknown the total amount of analyte present in the sample. Because recent advances in microwave vessel design (e.g., better pressure control and programmable temperature control) have allowed for the use of larger samples, microwave dissolution is becoming an important tool in the radiochemistry laboratory. Leaching and the newer closed-vessel microwave methods provide assurance that only minimal analyte loss will occur through volatilization.

Because of the potential for injury and explosions during sample treatment, 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. Review the Material Data Safety Sheets for all chemicals before their use.

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 sample dissolution (e.g., Bock, 1979; Bogen, 1978; Dean, 1995; Sulcek and Povondra, 1989).

13.2   The Chemistry of Dissolution

In order to dissolve a sample completely, each insoluble component must be converted into a soluble form. Several different chemical methods may need to be employed to dissolve a sample completely; usually, the tracer is added to the sample at the time of sample dissolution. Initially the sample may be treated with acids yielding an insoluble residue. The residue may need to be dissolved using fusion or hydrofluoric acid (HF) and then combined with the original mixture or analyzed separately. In either case, the tracer/carrier should be added to the sample during the first step of chemical change (e.g., acid dissolution as above) so that the yield for the entire process may be determined accurately. An outline of the principles of these chemical methods is provided in this section, but a complete description is available in Chapter 14, 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 sometimes used. 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. The solubility may be 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"). For example, the solubility product constant for strontium carbonate, a highly insoluble salt (0.0006 g/100 mL), is the equilibrium constant for the process:

$$SrCO_3(s) \rightarrow Sr^{+2}(aq) + CO_3^{-2}(aq)$$
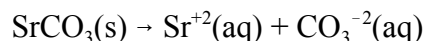
and is represented by:

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

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 reagents 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:

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

$$H_2CO_3 \rightarrow CO_2 + H_2O$$
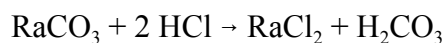
and the net reaction is as follows:

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

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; Steinberg, 1960):

$$ZrO_2 + 2\,Na_2S_2O_7 \rightarrow 2\,Na_2SO_4 + Zr(SO_4)_2$$
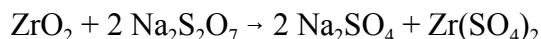
Many environmental samples contain insoluble silicates, such as aluminum silicate [$Al_2(SiO_3)_3$ or $Al_2O_3 \cdot 3SiO_2$], which can be converted into soluble silicates by fusion with sodium carbonate:

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

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 are an extremely important aspect of sample dissolution. The analyte may be present in a sample in several different chemical forms or oxidation states. As an example, consider a ground-water sample that contains ^{129}I as the analyte. The iodine may be present in any of the following inorganic forms: I^-, I_2, IO^-, or IO_3^-. If the ground water has a high reduction potential or certain bacteria are present, the iodine also may be present as CH_3I. It is of paramount importance to ensure that all of these different forms of iodine are brought to the same oxidation state (e.g., to iodate) at the time of first change in redox environment or change in sample composition. Furthermore, accurate assessment of chemical yield only can be determined if the tracer or carrier is added prior to a change in chemical form or oxidation state of the analyte at an initial point in the digestion process. This process is referred to as "equilibration of the tracer/carrier and analyte." From this point on during the sample analysis, any loss that occurs to the analyte will occur to an equal extent for the tracer/carrier, thus allowing the calculation of a chemical yield for the process.

A redox reaction 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 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 its elemental form.) Dissolution of uranium for analysis is an example of hydrogen-ion displacement to produce a soluble substance (Grindler, 1962):

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

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 with a negative standard reduction potential will replace hydrogen and be dissolved. Perchloric acid offers a particular advantage because very soluble metal 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 state is common when dissolving uranium samples in acids or during treatment with fusion fluxes. The uranyl ion (UO_2^{+2}) forms soluble salts—such as chloride, nitrate, and perchlorate—with anions of the common acids (Grindler, 1962). (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 pertechnetate salts (Cobble, 1964):

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

13.2.4 Complexation

The formation of complex ions (see also Section 14.3, "Complexation") is important in some dissolution processes, usually occurs in conjunction with treatment by an acid, and also can occur during fusion. Complexation increases solubility in the dissolution mixture and helps to minimize hydrolysis of the cations. 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). Numerous stable complexes of anions from solubilizing acids (HCl, HF, HNO_3, H_2SO_4, $HClO_4$) contribute to the dissolution of other elements, such as americium, cobalt, technetium, thorium, uranium, and zirconium (see Section 14.10, "Analysis of Specific Radionuclides"). 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).

13.2.5 Equilibrium: Carriers and Tracers

Carriers and tracers that are sometimes required for radiochemical separation 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 equilibrium with the analyte. The dissolution process tends to bring the carriers and tracers to the same oxidation state as the analyte and ensures complete 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 radioactive equilibrium are found in Section 14.9, "Carriers and Tracers," Section 14.10, "Analysis of Specific Radionuclides," and Attachment 14A, "Radioactive Decay and Equilibrium." The immediate and final forms of these tracers, carriers, and analytes are crucial information during the analytical process. During each of the steps in a given separation 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 possible interactions. 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 employed most often for samples that are difficult to dissolve in acids such as soils, sludges, silicates, and some metal oxides. Fusion is accomplished by heating a salt (the flux) mixed with an appropriate 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, acid treatment, 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. Samples with significant amounts of organic material are typically dry ashed or wet ashed before fusion. Solid samples are ground to increase the surface area, allowing the fusion process to proceed more readily. The sample must be mixed thoroughly 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.

During fusion, samples 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.

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	250°	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_2 (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).

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 sometimes 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 remove and 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 most 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 HNO_3, by hand cleaning with sea sand or by performing a blank fusion with sodium hydrogen sulfate.

Many kinds of salts are used in 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). Pyrosulfate fusions are prepared routinely in the laboratory by heating a mixture of sodium or potassium sulfate with a stoichiometric excess of sulfuric acid:

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

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

$$Na_2SO_4 \text{ etc.}$$
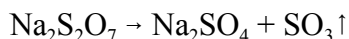
The rate of heating is increased with time until the sulfuric acid has volatilized and a clear pyrosulfate fusion is obtained. A pyrosulfate melt can be reprocessed if necessary to achieve complete sample dissolution. The analyst must distinguish between insoluble material that has not yet or will not 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 due to 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. Volatility could be a problem at these temperatures. Mercury and thallium are lost completely, while selenium, arsenic, and iodine suffer considerable losses. Nonsilicate samples should be dissolved in water, while silicate samples should be treated with acid (Bock, 1979).

Platinum crucibles are recommended for fusion of solid samples 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.

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

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

LITHIUM METABORATE ($Li_2B_4O_7$) is well-suited for dissolving basic oxides, such as alumina (Al_2O_3), quicklime (CaO), and silicates. Platinum dishes are normally used for this type of fusion, but occasionally graphite crucibles are advantageous because they can be heated rapidly by induction, and because they are not wetted by $Li_2B_4O_7$ melts. The fusion melt typically is dissolved in dilute acid, usually nitric but sometimes sulfuric. When easily hydrolyzed metal ions are present, dissolution should be carried out in the presence of ethylenediamine tetracetic acid (EDTA) or its di-sodium salt in 0.01 M HCl (Bock, 1979).

LITHIUM METABORATE ($LiBO_2$), or a mixture of the meta- and tetraborates, is a more basic flux and is better for dissolving highly acidic oxides or very insoluble ones, such as silica (SiO_2) or rutile (TiO_2). The metaborate is, however, suitable for dissolving all metal oxides. After the melt of sample and metaborate are dissolved, hydrogen peroxide should be used to maintain the titanium in solution.

13.3.3 Fluoride Fusions

Fluoride fusions are used for the removal of silicon, the destruction of silicates and rare earth minerals, and the analysis of oxides of niobium, tantalum, titanium, and zirconium. Sill et al. (1974) and Sill and Sill (1995) describe a method using potassium fluoride/potassium pyrosulfate fusion for determining alpha-emitting nuclides in soil (see Section 13.8, "Comparison of Total Dissolution and Acid Leaching"). Sulcek and Povondra (1989) describe the isolation of the rare earth elements 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 (rare earths + Th + Ca + U) are filtered out, dissolved, and further separated.

Platinum crucibles are recommended for fluoride fusions. Silicon, boron, lead, and polonium 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.

13.3.4 Sodium Hydroxide Fusion

Burnett et al. (1997) presented a technique that employs sodium hydroxide as the fusion agent in a 5:1 ratio to the soil. The fusion is performed in an alumina crucible, and deionized water is added to the resultant cake. Sufficient iron exists in most samples to from an $Fe(OH)_3$ scavenging precipitate for the actinides. The addition of sodium formaldehyde sulfoxylate ("Rongalite") ensures all actinides are in the +4 or +3 valence state.

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 decompose all types of samples completely. 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).

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^{+4} oxide and Hg^{+2} 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.

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

Half-Reaction	E^0 (volts)	Half-Reaction	E^0 (volts)
$Ag^{2+} + e^- \rightarrow Ag^+$	1.980	$I_3^- + 3e^- \rightarrow 3I^-$	0.536
$S_2O_8^{2-} + 2e^- \rightarrow 2SO_4^{2-}$	1.96	$I_2 + 2e^- \rightarrow 2I^-$	0.536
$Ce^{4+} + e^- \rightarrow Ce^{3+}$	1.72	$Cu^+ + e^- \rightarrow Cu$	0.53
$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2$ (s) $+ 2H_2O$	1.70	$4H_2SO_3 + 4H^+ + 6e^- \rightarrow S_4O_6^{2-} + 6H_2O$	0.507
$2HClO + 2H^+ + 2e^- \rightarrow Cl_2 + 2H_2O$	1.630	$Ag_2CrO_4 + 2e^- \rightarrow 2Ag + CrO_4^{2-}$	0.449
$2HBrO + 2H^+ + 2e^- \rightarrow Br_2 + 2H_2O$	1.604	$2H_2SO_3 + 2H^+ + 4e^- \rightarrow S_2O_3^{2-} + 3H_2O$	0.400
$NiO_2 + 4H^+ + 2e^- \rightarrow Ni^{2+} + 2H_2O$	1.593	$UO_2^+ + 4H^+ + e^- \rightarrow U^{4+} + 2H_2O$	0.38
Bi_2O_4 (bismuthate) $+ 4H^+ + 2e^- \rightarrow 2BiO^+ + 2H_2O$	1.59	$Cu^{2+} + 2e^- \rightarrow Cu$	0.340
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	1.51	$VO^{2+} + 2H^+ + e^- \rightarrow V^{3+} + H_2O$	0.337
$2BrO_3^- + 12H^+ + 10e^- \rightarrow Br_2 + 6H_2O$	1.478	$BiO^+ + 2H^+ + 3e^- \rightarrow Bi + H_2O$	0.32
$PbO_2 + 4H^+ + 2e^- \rightarrow Pb^{2+} + 2H_2O$	1.468	$UO_2^{2+} + 4H^+ + 2e^- \rightarrow U^{4+} + 2H_2O$ ...	0.27
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$ ...	1.36	Hg_2Cl_2 (s) $+ 2e^- \rightarrow 2Hg + 2Cl^-$	0.2676
$Cl_2 + 2e^- \rightarrow 2Cl^-$	1.3583	$AgCl$ (s) $+ e^- \rightarrow Ag + Cl^-$	0.2223
$2HNO_2 + 4H^+ + 4e^- \rightarrow N_2O + 3H_2O$	1.297	$SbO^+ + 2H^+ + 3e^- \rightarrow Sb + H_2O$	0.212
$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$	1.23	$CuCl_3^{2-} + e^- \rightarrow Cu + 3Cl^-$	0.178
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	1.229	$SO_4^{2-} + 4H^+ + 2e^- \rightarrow H_2SO_3 + H_2O$ ..	0.158
$ClO_4^- + 2H^+ + 2e^- \rightarrow ClO_3^- + H_2O$	1.201	$Sn^{4+} + 2e^- \rightarrow Sn^{2+}$	0.15
$2IO_3^- + 12H^+ + 10e^- \rightarrow I_2 + 3H_2O$	1.19	$CuCl + e^- \rightarrow Cu + Cl^-$	0.121
$N_2O_4 + 2H^+ + 2e^- \rightarrow 2HNO_2$	1.07	$TiO^{2+} + 2H^+ + e- \rightarrow Ti^{3+} + H_2O$	0.100
$2ICl_2^- + 2e^- \rightarrow 4Cl^- + I_2$	1.07	$S_4O_6^{2-} + 2e^- \rightarrow 2S_2O_3^{2-}$	0.08
Br_2 (aq) $+ 2e^- \rightarrow 2Br^-$	1.065	$2H^+ + 2e^- \rightarrow H_2$	0.0000
$N_2O_4 + 4H^+ + 4e^- \rightarrow 2NO + 2H_2O$	1.039	Hg_2I_2 (s) $+ 2e^- \rightarrow 2Hg + 2I^-$	-0.0405
$HNO_2 + H^+ + e^- \rightarrow NO + H_2O$	0.996	$Pb^{2+} + 2e^- \rightarrow Pb$	-0.125
$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$	0.957	$Sn^{2+} + 2e^- \rightarrow Sn$	-0.136
$NO_3^- + 3H^+ + 2e^- \rightarrow HNO_2 + H_2O$	0.94	AgI (s) $+ e^- \rightarrow Ag + I^-$	-0.1522
$2Hg^{2+} + 2e^- \rightarrow Hg_2^{2+}$	0.911	$V^{3+} + e^- \rightarrow V^{2+}$	-0.255
$Cu^{2+} + I^- + e^- \rightarrow CuI$ (s)	0.861	$Ni^{2+} + 2e^- \rightarrow Ni$	-0.257
OsO_4 (s) $+ 8H^+ + 8e^- \rightarrow Os + 4H_2O$	0.84	$Co^{2+} + 2e^- \rightarrow Co$	-0.277
$Ag^+ + e^- \rightarrow Ag$	0.7991	$PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$	-0.3505
$Hg_2^{2+} + 2e^- \rightarrow 2Hg$	0.7960	$Cd^{2+} + 2e^- \rightarrow Cd$	-0.4025
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.771	$Cr^{3+} + e^- \rightarrow Cr^{2+}$	-0.424
$H_2SeO_3 + 4H^+ + 4e^- \rightarrow Se + 3H_2O$	0.739	$Fe^{2+} + 2e^- \rightarrow Fe$	-0.44
$HN_3 + 11H^+ + 8e^- \rightarrow 3NH_4^+$	0.695	$H_3PO_3 + 2H^+ + 2e^- \rightarrow HPH_2O_2 + H_2O$	-0.499
$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$	0.695	$U^{4+} + e^- \rightarrow U^{3+}$	-0.52
$Ag_2SO_4 + 2e^- \rightarrow 2Ag + SO_4^{2-}$	0.654	$Zn^{2+} + 2e^- \rightarrow Zn$	-0.7626
$Cu^{2+} + Br^- + e^- \rightarrow CuBr$ (s)	0.654	$Mn^{2+} + 2e^- \rightarrow Mn$	-1.18
$2HgCl_2 + 2e^- \rightarrow Hg_2Cl_2$ (s) $+ 2Cl^-$	0.63	$Al^{3+} + 3e^- \rightarrow Al$	-1.67
$Sb_2O_5 + 6H^+ + 4e^- \rightarrow 2SbO^+ + 3H_2O$	0.605	$Mg^{2+} + 2e^- \rightarrow Mg$	-2.356
$H_3AsO_4 + 2H^+ + 2e^- \rightarrow HAsO_2 + 2 H_2O$	0.560	$Na^+ + e^- \rightarrow Na$	-2.714
$TeOOH^+ + 3H^+ + 4e^- \rightarrow Te + 2H_2O$	0.559	$K^+ + e^- \rightarrow K$	-2.925
$Cu^{2+} + Cl^- + e^- \rightarrow CuCl$ (s)	0.559	$Li^+ + e^- \rightarrow Li$	-3.045
		$3N_2 + 2H^+ + 2e^- \rightarrow 2HN_3$	-3.1

Source: Dean, 1995.

Oxidizing acids, such as nitric acid, hot concentrated sulfuric acid, or hot concentrated perchloric acid, are used to dissolve metals whose E^0 values are greater than 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:

$$SiO_2 + 6HF \rightarrow H_2SiF_6 + 2H_2O$$
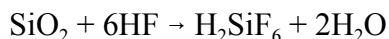
whereby the fluorosilicic acid formed dissociates into gaseous silicon tetrafluoride and hydrogen fluoride upon heating:

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

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 IV to VI 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).

HF should never be used or stored in glass, or porcelain containers. Digestion in platinum containers is preferred, and Teflon™ is acceptable as long as the temperature does not exceed 250 °C. This would occur only with HF if the mix were taken to dryness, because the constant boiling azeotrope is 112 °C. HF works most effectively when used alone, as all other acids or oxidizing agents used are less volatile than HF and would cause the HF concentration to be decreased at elevated temperatures. HF is most effective when used on a solid residue. Samples should be ground to a fine powder to increase the surface area and moistened with a minimal

amount of water to prevent losses as dust and spray when the acid is added to the sample. After the addition of HF, the sample may be allowed to react overnight to dissolve the silicates. However, heating the solution to 80 °C will allow reaction to occur within 1-2 hours. Because it is such a strong complexing agent, excess fluoride ion can cause problems with many separation methods. 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 boric acid or sodium tetraborate. The fluorides are converted to BF_3 that is then removed by evaporation.

HYDROCHLORIC ACID (HCl) is one of the most widely used acids for sample dissolution 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 Au^{+3}, Ti^{+3}, and Hg^{+2}. The concentrated acid will also complex Fe^{+3}, Ga^{+3}, In^{+3}, and Sn^{+4}. 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(+4) ratio. The so-called uranium blacks with minimal contents of U(+4) 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."

As^{+3}, Sb^{+3}, Ge^{+3}, and Se^{+4} are volatilized easily in HCl solutions, while Hg^{+2}, Sn^{+4}, and Rh(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 sample dissolution. HBr forms an azeotrope with water containing 47.6 percent by weight 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. Solutions often appear yellowish-brown because of the formation of the triiodide complex (I^-_3). HI is most often used as a reducing agent during dissolutions. HI also dissolves Sn^{+4} oxide, and complexes and dissolves Hg^{+2} sulfide. HI forms an azeotrope with water containing 56.9 percent by weight 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.

Non-fuming H_2SO_4 does not exhibit oxidizing properties, but the concentrated acid will dissolve many elements and react with almost all organic compounds. Concentrated sulfuric acid is a powerful dehydrating agent. Its action on organic materials is a result of removing OH and H groups (to form water) from adjacent carbon atoms. This forms a black char (residue) that is not easily dissolved using wet-ashing techniques. 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™ should not be used above 250 °C, and, therefore, it is not recommended for applications involving concentrated H_2SO_4 that require elevated temperature.

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 separation 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 an adherent layer of insoluble oxide when treated with HNO_3, thereby passivating the metal surface. 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 also 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 bismuth metal and alloys with concentrated acid.
• Dissolving metals (e.g., steel) in concentrated acid when gaseous hydrogen is heated.
• Heating uranium turnings or powder in concentrated acid.
• Heating finely divided aluminum and silicon in concentrated acid.
• Heating antimony or Sb^{+3} 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 contact 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 standard operating procedure that must be followed exactly to ensure the safety of the analyst (Schilt, 1979).

AQUA REGIA. One part concentrated HNO_3 and three parts concentrated HCl (by 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 U^{+4} 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 Mn^{+2} 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 as a strong oxidizing agent to dissolve carbonaceous compounds. The Cr^{+3} 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.

13.5 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 an important radiochemical tool (Smith and Yaeger, 1996; Alvarado et al., 1996). A series of articles in *Spectroscopy* describes recent advances in microwave dissolution technology (Kammin and Brandt, 1989; Grillo, 1989 and 1990; Gilman and Engelhardt, 1989; Lautensch-lager, 1989; Noltner et al., 1990), and Dean (1995) presents a synopsis of current microwave theory and technology. Kingston and Jassie (1988) and Kingston and Haswell (1997) are other excellent resources for this topic.

The American Society for Testing and Materials (ASTM) has issued several protocols for various media. ASTM D5258 describes the decomposition of soil and sediment samples for subsequent analyte extraction; ASTM D4309 addresses the decomposition of surface, saline, domestic, and industrial waste water samples; and 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 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. 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 (689 to 2,068 kPa), depending on the model thereby limiting the size of organic samples utilized. However, inorganic materials such as metals, water and waste waters, minerals, and most soils and sediments are easily digested without generating large amounts of gaseous by-products. Typical sample sizes are on the order of 0.5 g for solids and 45 mL for aqueous samples.

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

13.5.3 High-Pressure, Closed-Vessel Systems

Recent advances in vessel design have produced microwave vessels capable of withstanding pressures on the order of 1,500 psi (10 mPa; Lautenschlager, 1989), allowing for larger sample sizes on the order of 1 to 2 g for soil (Smith and Yaeger, 1996) or 0.5 to 3 g for vegetation (Alvarado et al., 1996) and, consequently, better detection limits. These high-pressure vessels are used to digest organic and inorganic substances, such as coals, heavy oils, refractories, and ceramic oxides, which cannot easily be digested with other techniques. Additionally, vessel composition continues to improve. Noltner et al. (1990) have demonstrated that

Tetrafluorometoxil™ (TFM) vessels exhibit significantly lower blank background values from residual contamination and reuse than vessels produced with the more traditional PFA. This lower "memory" results in lower detection limits, a clear advantage for environmental laboratories.

13.6 Verification of Total Dissolution

Following aggressive acid digestion or fusion, the analyst often must determine if the sample has indeed been dissolved. This determination is made first through visual inspection for particulate matter in the acid leachate, post-digestion solution, or dissolved fusion melt. (The analyst should allow the solution to cool prior to making an assessment of total dissolution.) A hot digestate may appear to be free from particulate matter. However, upon cooling, finely divided particulate or colloidal matter may agglomerate, forming a residue. If a residue is observed, this residue must be physically separated, or the sample digestate must be retreated to ensure a single final aqueous phase. Sometimes these residues are inconsequential and contain no analyte of interest. Project-specific requirements will dictate how these residues are handled.

If no particles are readily observed, small undissolved particles that are invisible to the unaided eye may be present. A method to assess this may be to filter a duplicate cooled solution (see Section 10.3.2, "Liquid Sample Preparation: Filtration") and count it using a gamma spectrometer, alpha spectrometer, or proportional counter. The analyst should focus on the analytes of interest to assess whether any activity is lost in this residue. Finally, for those cases where the laboratory has decided to perform an acid leaching, rather than a total dissolution or fusion, it is advisable to perform 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 leaching approach is adequate for the particular sample matrix.

13.7 Special Matrix Considerations

13.7.1 Liquid Samples

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

Most radiochemical analyses are performed in aqueous solutions. Because nonaqueous liquids are incompatible with this requirement, these samples must be converted into an aqueous form. In most cases, the nonaqueous liquid is simply a solvent that does not contain the radionuclide of interest, and the nonaqueous solvent simply can be removed and the residue dissolved as described in Sections 13.3 ("Fusion Techniques") and 13.4 ("Wet Ashing and Acid Dissolution Techniques").

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

13.7.2 Solid Samples

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

13.7.3 Filters

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

13.7.4 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).

13.8 Comparison of Total Dissolution and Acid 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, Appendix II, Method 1311), which are intended to determine the leachability of a nonradioactive analyte.

"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, as indicated by Sill and Sill (1995), this may not always be possible:

"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."

Thus, the results of acid leaching processes should be used with caution.

There are those within the radiochemistry community who contend that total sample dissolution provides the most analytically accurate and reproducible analyte concentration in the sample. Sill and Sill (1995), longtime proponents of total dissolution, state:

"Any procedure that fails to obtain complete sample dissolution …will inevitably give low and erratic results. 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."

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, single-sample processing requires a dedicated analyst. 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 some fusion processes increase the danger of loss of certain analytes by volatilization. Finally, the crucible itself may be 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 this sample is representative.

13.9 References

13.9.1 Cited References

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14 SEPARATION TECHNIQUES

14.1 Introduction

The methods for separating, collecting, and detecting 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).

While separation techniques and principles may be found in standard textbooks, Chapter 14 addresses the basic chemical principles that apply to the analysis of radionuclides, with an emphasis on their unique behavior. It is not a comprehensive review of all techniques. This chapter provides: (1) a review of the important chemical principles underlying radiochemical separations, (2) a survey of the important separation methods used in radiochemistry with a discussion of their advantages and disadvantages, and (3) an examination of the particular features of radioanalytical chemistry that distinguish it from ordinary analytical chemistry. Extensive examples have been provided throughout the chapter to illustrate various principles, practices, and procedures in radiochemistry. Many were selected purposely as familiar illustrations from agency procedural manuals. Others were taken from the classical and recent radiochemical literature to provide a broad, general overview of the subject.

This chapter integrates the concepts of classical chemistry with those topics unique to radio-nuclide analysis. The first eight sections of the chapter describe the bases for chemical separations involving oxidation-reduction, complex-ion formation, distillation/volatilization, solvent extraction, precipitation and coprecipitation, electrochemistry, and chromatography. Carriers and tracers, which are unique to radiochemistry, are described in Section 14.9 together with specific separation examples for each of the elements covered in this manual. Section 14.10 also provides an overview of the solution chemistry and appropriate separation techniques for 17 elements. An attachment at the end of the chapter describes the phenomenon of radioactive equilibrium, also unique to radioactive materials.

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 its own with a counter-ion requires judicious

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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 often can 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 digestion or slow filtration 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, chemical effects of the radiation, such as decomposition of solvents (through radiolysis) and heat effects (caused by interaction of decay particles with the solution), can affect the procedures. Equally important, even at lower activity levels, is the radiation dose that the radiochemist can receive unless protected by shielding, ventilation, time, 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 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 (see Chapter 17, *Waste Management in a Radioanalytical Laboratory*).

The past 10 years have seen significant improvements to some of the classical techniques as well as the development of new methods of radiochemical analysis. Knowledge of these analytical developments, as well as maintenance of a working familiarity with developing techniques in the radiochemistry field will further enhance the waste reduction effort.

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. There must be complete equilibration (isotopic exchange) between the added isotope(s) and all the analyte species present in order to achieve quantitative yields. The oxidation number of a radionuclide can affect its chemical stability in the presence of water, oxygen, and other natural substances in solution; reactivity with reagents used in the radioanalytical procedure; solubility in the presence of other ions and molecules; and 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 they will exhibit the same chemical behavior during radiochemical analysis (i.e., no mass isotope effects).

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 solution. 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:

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

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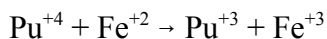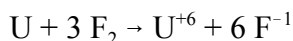
In the first reaction, uranium loses electrons, becoming a cation (oxidized), and fluorine gains an electron (reduced), becoming an anion. In the second reaction, the reactants are already ions, but the plutonium cation (Pu^{+4}) gains an electron, becoming Pu^{+3} (reduced), and the ferrous ion (Fe^{+2})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

In other redox reactions, electrons are not completely transferred from one reacting species to another; the electron density of one atom decreases while it increases at another atom. The change in electron density occurs as covalent bonds (in which electrons are shared between two atoms) are broken or 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 electro-negative 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 is oxidized to carbon dioxide by oxygen:

$$C + O_2 \rightarrow CO_2$$
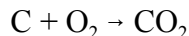
the electron density associated with the carbon atom decreases, and that of the oxygen atoms increases, because the electronegativity of oxygen is greater than the electronegativity of carbon. In this example, carbon is oxidized and oxygen is reduced. Another example from the chemistry of the preparation of gaseous uranium hexafluoride (UF_6) illustrates this type of redox reaction:

$$3 \ UF_4 + 2 \ ClF_3 \rightarrow 3 \ UF_6 + Cl_2$$
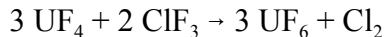
Because the order of electronegativity of the atoms increases in the order U < Cl < F, the uranium atom in uranium tetrafluoride (UF_4) is oxidized further as more electronegative fluorine atoms are added to the metal and shift the electron density away from uranium. Chlorine atoms break their bonds with fluorine and gain electron density (are reduced) when 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 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 electrons or by unequal sharing of electrons in a covalent bond. The number increases as the electron density decreases, and 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 polyatomic molecules. 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; 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. For example, all oxygen in sulfate are −2. (A specific exception is 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. 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 Group IA elements, Li, Na, K, Rb, Cs, and Fr) have an oxidation number of +1; the alkaline earth metals (the Group IIA elements, Be, Mg, Ca, Sr, Ba, and Ra) have an oxidation number of +2.

3. Fluorine has an oxidation number of −1; hydrogen has an oxidation number of +1.

4. Oxygen has an oxidation number of −2.

5. The halogens (the Group 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 Group VIA elements, O, S, Se, Te, and Po) is −2; for the nitrogen family of elements (the VA elements except 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 the net charge on the molecule is zero. 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 or those of polyatomic ions, such as chromium(VI) in CrO_4^{-2}. In general, elements in solution whose oxidation number is greater than +4 or less than -4 can exist only as complexed ions in solution. Many of the transuranic elements can occur in multiple oxidation states, and the transformation from one to another is a critical step of the separation process. In this chapter, all species whose oxidation number is greater than +4 will be represented either by their complexed form in solution or by its symbol with a Roman numeral signifying the oxidation state [UO_2^+ or U(V)]. This conforms to the intent of IUPAC (1990) nomenclature.

14.2.3 Common Oxidation States

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 it is bonded to fluorine (where it can be +1 or +2); in peroxides, where the oxidation state is -1; or in superoxides, where it is -½.

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

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). 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 occur. The (VII) and +4 ions behave very differently in solution. For instance, pertechnetate does not coprecipitate with ferric hydroxide, while Tc^{+4} does.

The oxidation states of the actinide elements have been comprehensively discussed by Ahrland (1986) and Cotton and Wilkinson (1988). 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, americium, and curium. The +4 state is common for thorium and plutonium, whereas (V) is most common for protactinium and neptunium. The most stable state for uranium is the (VI) oxidation state.

In compounds of the +3 and +4 oxidation states, the elements are present as simple M^{+3} or M^{+4} cations (where "M" is the metal ion); 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, and 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(V). 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(VI). This 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, (V), and (VI), 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 Coleman (1965). According to Cleveland (1970), this polyvalent behavior occurs because of the tendency of Pu^{+4} and Pu(V) to disproportionate:

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

$$3\ PuO_2^{+1} + 4\ H^{+1} \rightarrow Pu^{+3} + 2\ PuO_2^{+2} + 2\ H_2O$$
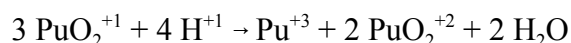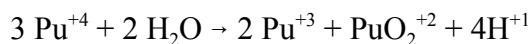
and because of the slow rates of reaction involving formation or rupture of Pu-O bonds (such as PuO_2^{+} and PuO_2^{2+}) compared to the much faster reactions involving only electron transfer. The distribution depends on the type and concentration of acid used for dissolution, the method of solution 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) 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(V)	~0.7%
Pu(VI)	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. At high levels, 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, "Analysis of Specific Radionuclides").

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.

<center>TABLE 14.1 — Oxidation states of elements</center>

Element	Oxidation State[1]	Chemical Form	Notes[2]
Am	**+3**	Am^{+3}	Pink; stable; difficult to oxidize
	+4	Am^{+4}	Pink-red; unstable in acid
	(V)	AmO_2^{+1}	Pink-yellow; disproportionates in strong acid; reduced by products of its own radiation
	(VI)	AmO_2^{+2}	Rum color; stable

Element	Oxidation State[1]	Chemical Form	Notes[2]
Cs	+1	$Cs(H_2O)_x^{+1}$	Colorless; x probably is 6
Co	**+2** +3	$Co(H_2O)_6^{+2}$ $Co(H_2O)_6^{+3}$	Pink to red; oxidation is very unfavorable in solution Rapidly reduced to +2 by water unless acidic
Fe	+2 **+3**	$Fe(H_2O)_6^{+2}$ $Fe(H_2O)_6^{+3}$	Green Pale yellow; hydrolyses in solution to form yellow or brown complexes
^{3}H	+1	^{3}HOH and $^3HOH_2^{+1}$	Isotopic exchange of tritium is extremely rapid in samples that have water introduced.
I	**−1** -1/3 +1 (V) (VII)	I^{-1} I_3^{-1} OI^{-1} IO_3^{-1} IO_4^{-1}	Colorless Brown; commonly in solutions of I^{-1} exposed to air Colorless Colorless; formed in vigorously oxidized solutions Colorless
Ni	+2	$Ni(H_2O)_6^{+2}$	Green
Nb	+3 **+5**	Unknown $HNb_6O_{19}^{-7}$	In sulfuric acid solutions of Nb_2O_5
Po	+4		
Pu	+3 **+4** (V) (VI) (VII)	$Pu(H_2O)_x^{+3}$ $Pu(H_2O)_x^{+4}$ $Pu(H_2O)_x^{+5}$ or PuO_2^{+1} PuO_2^{+2} PuO_5^{-3} or $PuO_4(OH)_2^{-3}$	Violet to blue; stable to air and water; easily oxidized to +4 Tan to brown; first state formed in freshly prepared solutions; stable in 6 M acid; disproportionates in low acidity to +3 and +6 Never observed alone; always disproportionates; most stable in low acidity Purple Yellow-pink; stable but fairly easy to reduce Green $PuO_4(OH)_2^{-3}$ 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 (V) **(VII)**	TcO_3^{-2} TcO_3^{-1} TcO_4^{-1}	
Th	+4	$Th(H_2O)_8^{+4}$	Colorless; at pH>3 forms complex hydrolysis products
U	+3 **+4** (V) (VI)	$U(H_2O)_x^{+3}$ $U(H_2O)_{8\ or\ 9}^{+4}$ UO_2^{+1} $UO_2(H_2O)_5^{+2}$	Red-brown; slowly oxidized by water and rapidly by air to +4 Green; stable but slowly oxidized by air to (VI) Unstable but more stable at pH 2-4; disproportionates to +4 and (VI) Yellow; only form stable in solution containing air; difficult to reduce
Zr	+4	$Zr(H_2O)_6^{+4}$ $Zr_4(OH)_8(H_2O)_{16}^{+2}$	Only at very low ion concentrations and high acidity At typical concentrations in absence of complexing agents

(1) Most common form is in bold.
(2) Color shades may vary depending on the concentration of the isotope.
   Sources: Booman and Rein, 1962; Cotton and Wilkinson, 1988; Emsley, 1989; Greenwood and Earnshaw, 1984; Grinder, 1962; Hampel, 1968; Katzin, 1986; Latimer, 1952; and 1970.

TABLE 14.2 — Oxidation states of selected elements

Element	+1	+2	+3	+4	V	VI	VII	VIII
Titanium		○	○	●				
Vanadium		○	○	●	●			
Chromium		●	●	○	○	●		
Manganese		●	○	●	○	○	●	
Iron		●	●	○		○		
Cobalt		●	●					
Nickel		●	○	○				
Strontium		●						
Yttrium			●					
Molybdenum		○	○	●	●	●		
Technetium		○	○	●	○	○	●	
Silver	●		○	○				
Cesium	●							
Barium		●						
Lanthanides			●					
Lead		●		○				
Polonium		○		●		○		
Radium		●						
Actinium			●					
Thorium				●				
Protactinium				○	●			
Uranium			○	○	○	●		
Neptunium			○	○	●	○	○	
Plutonium			○	●	○	○		
Americium			●	○	○	○		
Curium			●	○				

The stable nonzero oxidation states are indicated. The more common oxidation states are indicated by solid black circles.
Sources: 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:

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

The magnitude of the equilibrium constant reflects the instability of the (V) 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:

$$H_2O_2 + 2H^{+1} + 2Fe^{+2} \rightleftharpoons 2H_2O + 2Fe^{+3}$$
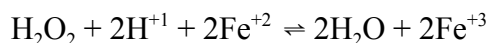
Hydrogen peroxide is frequently employed to oxidize Tc^{+4} to the pertechnetate:

$$4\ H_2O_2 + Tc^{+4} \rightleftharpoons TcO_4^{-1} + 4H_2O$$
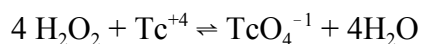
Hydrogen peroxide can also serve as a reducing agent, with an increase in oxidation state from -1 to 0, and the liberation of molecular oxygen. For example, hydrogen peroxide will reduce permanganate ion (MnO_4^{-1}) in basic solution, forming a precipitate of manganese dioxide:

$$2\ MnO_4^{-1} + 3\ H_2O_2 \rightarrow 2\ MnO_2\downarrow + 3\ O_2\uparrow + 2\ H_2O + 2\ OH^{-1}$$
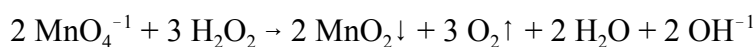
Furthermore, hydrogen peroxide can decompose by the reaction:

$$2\ H_2O_2 \rightarrow 2\ H_2O + O_2$$
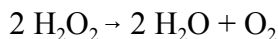
This reaction is another example of a disproportionation (auto-oxidation-reduction) in which a chemical species acts simultaneously as an oxidizing and reducing agent; half of the oxygen atoms are reduced to O^{-2}, and the other half are oxidized to elemental oxygen (O^0) in the diatomic state, O_2.

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}:

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

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

$$MnO_4^{-1} + 3\ e^{-1} + 4\ H^{+1} \rightarrow MnO_2 \downarrow + 2\ H_2O$$
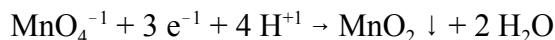
These oxidizing agents are discussed further in Section 13.4, "Wet Ashing and Acid Dissolution Techniques."

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(VI) 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(VI) $\rightarrow$ 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 13.4, "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(V) to Np^{+4} and Pu^{+4} to Pu^{+3} in acidic media.

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 used frequently to reduce Fe^{+3} to Fe^{+2} to remove this interference. Ascorbic acid is also used to reduce Pu^{+4} to Pu^{+3}.

SULFAMIC ACID. Aqueous solutions of this solid material are strongly acidic and act selectively as oxidizing agents. It is of particular value in its ability to oxidize nitrites to nitrates while not affecting Pu^{+3} or Np^{+4} ions.

14.2.6 Oxidation State and Radiochemical Analysis

Most radiochemical analyses require the radionuclide be in aqueous solution. Thus, 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, and chemical equilibration with tracers or carriers can be established. 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 to Table 14.1, page 14-9). 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 radionuclide 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.

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

TABLE 14.3 — Redox reagents for radionuclides[1]

Redox Reaction	Reagent	Conditions
$Am^{+3} \rightarrow AmO_2^{+2}$	Ag^{+2}, $Ag^+/S_2O_8^{-2}$	
$Am^{+4} \rightarrow AmO_2^{+2}$	O_3	13 M NH_4F
$AmO_2^{+1} \rightarrow AmO_2^{+2}$	Ce^{+4}	$HClO_4$
	O_3	Heated HNO_3 or $HClO_4$
$AmO_2^{+2} \rightarrow AmO_2^{+1}$	Br^{-1}, Cl^{-1}	
	Na_2CO_3	Heat to precipitate $NaAmO_2CO_3$; dissolve in H^{+1}
$AmO_2^{+2} \rightarrow Am^{+3}$	I^{-1}, H_2O_2, NO_2^{-1}, SO_2	
$Am^{+4} \rightarrow Am^{+3}$	alpha radiation effects	Spontaneous
$Co^{+2} \rightarrow Co^{+3}$	O_3	Cold $HClO_4$
	O_2, H_2O_2	Complexed cobalt
$Co^{+3} \rightarrow Co^{+2}$	H_2O	Rapid with evolution of H_2
$Fe^{+2} \rightarrow Fe^{+3}$	O_2	Faster in base; slower in neutral and acid solution; decreases with H^{+1}
	Ce^{+4}, MnO_4^{-1}, NO_3^{-1}, H_2O_2, $S_2O_8^{-2}$	
	$Cr_2O_7^{-2}$	HCl or H_2SO_4

Redox Reaction	Reagent	Conditions
$Fe^{+3} \rightarrow Fe^{+2}$	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
$I^{-1} \rightarrow I_2$	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; $Na_2S_2O_3$	
$I^{-1} \rightarrow IO_3^{-1}$	$KMnO_4$	
	50% CrO_3 in 9M H_2SO_4	
$I^{-1} \rightarrow IO_4^{-1}$	NaClO in base	
$IO_4^{-1} \rightarrow I_2$	$NH_2OH \cdot HCl$	
	$H_2C_2O_4$	9 M H_2SO_4
$IO_4^{-1} \rightarrow I^{-1}$	$NaHSO_3$ in acid	
$I_2 \rightarrow I^{-1}$	SO_2; $NaHSO_3$	
$Np^{+3} \rightarrow Np^{+4}$		Dilute acid
$Np^{+4} \rightarrow NpO_2^{+1}$	NO_2^{-1}	HNO_3
$Np^{+4} \rightarrow NpO_2^{+2}$	MnO_4^{-1}	Dilute alkaline
$NpO_2^{+1} \rightarrow NpO_2^{+2}$		Acid
$NpO_2^{+2} \rightarrow NpO_5^{-3}$		Acid
$NpO_2^{+1} \rightarrow Np^{+4}$	Fe^{+2}	Dilute H_2SO_4
	Ti^{+3}	1–2 M HCl
$Pu^{+3} \rightarrow Pu^{+4}$	BrO_3^{-1}	Dilute H^{+1}
	Ce^{+4}	HCl or 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	
$Pu^{+4} \rightarrow PuO_2^{+2}$	$NaBiO_3$	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 dilute H_2SO_4/60°C
	Ag^{+2}	$Ag^{+1}/S_2O_8^{-1}$ in dilute 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^{-}	
$PuO_2^{+1} \rightarrow PuO_2^{+2}$	HNO_3	Dilute; slow
	V^{+3} or Ti^{+3}	$HClO_4$; slow
$PuO_2^{+2} \rightarrow PuO_2^{+1}$	I^{-1}	pH 2
	SO_2	H^{+1}

Redox Reaction	Reagent	Conditions
	Fe^{+2}	$HClO_4$ or HCl
	V^{+3} or U^{+4}	$HClO_4$
	HNO_2	Dilute HNO_3 $NaNO_3$
	Ag	Dilute HCl
$PuO_2^{+2} \rightarrow Pu^{+4}$	$C_2O_4^{-2}$	$75\,^\circ C$; RT with dilute 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 $75\,^\circ C$
	HNO_2	$HNO_3/75\,^\circ C$
	Zn	Dilute HCl
$PuO_2^{+1} \rightarrow Pu^{+4}$	HNO_2	Slow
	$NH_2OH \cdot HCl$	Dilute HCl, slow
$Pu^{+4} \rightarrow Pu^{+3}$	hydroquinone	Dilute HNO_3
	H_2/Pt	HCl
	I^{-1}	Dilute HCl
	HSO_3^{-1}	Dilute HNO_3
	$NH_2OH \cdot HCl$	
	Zn	Dilute HCl
	SO_2	Dilute HNO_3
	Ti^{+3}	HCl, dilute H_2SO_4, or dilute HNO_3/H_2SO_4
	ascorbic acid	HNO_3
	U^{+4}	Dilute $HClO_4$
	H_2S	Dilute acid
$Tc^{+4} \rightarrow TcO_4^{-1}$	HNO_3	
	H_2O_2	
	O_2 (air)	
TcO_2(hydrated) $\rightarrow$ TcO_4^{-1}	Ce^{+4}	
	H_2O_2	
$TcCl_6^{-2} \rightarrow TcO_4^{-1}$	H_2O_2	
	Cl_2	
	Ce^{+4}	
	MnO_4^{-1}	
$TcO_4^{-1} \rightarrow Tc^{+4}$ or TcO_2(hyd)	N_2H_4	Dilute H_2SO_4
	NH_2OH	Dilute H_2SO_4
	Ascorbic acid	Dilute H_2SO_4
	Sn^{+2}	Dilute H_2SO_4
	Zn	Dilute HCl
	Concentrated HCl	$\rightarrow TcCl_6^{-2}$
$U^{+3} \rightarrow U^{+4}$	ClO_4^{-1}	Dilute $HClO_4$
	Co^{+3} complexes	Dilute $HClO_4$ or $LiClO_4$

Redox Reaction	Reagent	Conditions
	Cr^{+3} and Cr^{+3} complexes	Dilute $HClO_4$ or $LiClO_4$
	H_2O	Dilute or concentrated HCl or H_2SO_4
	O_2 (air)	
$U^{+4} \rightarrow UO_2^{+2}$	Br_2	Catalyzed by Fe^{+3} or Mn^{+2}
	BrO_3^{-1}	$HClO_4$
	Ce^{+4}	Dilute $HClO_4$
	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	
	MnO_2	
$UO_2^{+1} \rightarrow UO_2^{+2}$	Fe^{+3}	
$UO_2^{+2} \rightarrow U^{+4}$	Cr^{+2}	
	Eu^{+2}	
	Np^{+3}	
	Ti^{+3}	
	V^{+2} and V^{+3}	
	Rongalite (an aqueous solution of sodium hydroxymethanesulfonate)	Dilute basic solution
$UO_2^{+2} \rightarrow U^{+3}$	Zn(Hg)	
$UO_2^{+1} \rightarrow U^{+4}$	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.

One method for the analysis of radioiodine 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, 1997, Method RP230). Iodine species in the water sample are first oxidized to iodate (IO_4^{-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 (VI) oxidation state is first reduced to +3 and +4 with Ti^{+3}, then uranium 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(VI) (as UO_2^{+2}) while being reduced, as follows:

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

$$(U^{+4} + 2\ Ce^{+4} + 2\ H_2O \rightarrow UO_2^{+2} + 2\ Ce^{+3} + 4\ H^{+1})$$
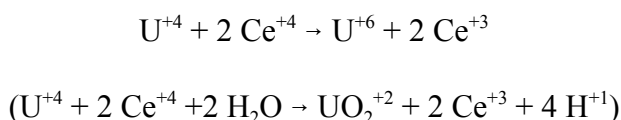
The excess Ce^{+4} is back-titrated with Fe^{+2} solution, using ferroin as indicator for the endpoint of the titration:

$$Fe^{+2} + Ce^{+4} \rightarrow Fe^{+3} + Ce^{+3}$$
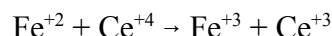
Electrochemical methods are typically used in radiochemistry to reduce ions in solution, plating them onto a target metal for counting. Americium ions (Am^{+3}) from soil samples ultimately are reduced from solution onto a platinum electrode by application of an electrical current in an electrolytic 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 and lead spontaneously deposit from a solution of hydrochloric acid onto a nickel disk at 85 °C (Blanchard, 1966). Alpha and beta counting are used to determine ^{210}Po and ^{210}Pb. Wahl and Bonner (1951) contains a table of electrochemical methods used for the oxidation and reduction of carrier-free tracers.

Oxidation-reduction chemistry often is used to separate mixtures of transuranics. This is because mixtures of several transuranics (e.g., U, Pu, Cm) or transition metals will generate different oxidation states of each element as a result of inter-element redox reactions. An example would be :

$$2 \ H_2O \ + \ U^{+4} \ + \ 2 \ Pu^{+4} \rightarrow UO_2^{2+} \ + \ 2 \ Pu^{+3} \ + \ 4 \ H^+$$
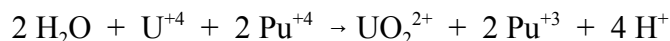
Thus, when attempting to determine plutonium (as the Pu^{+4} ion) in a solution containing U^{+4}, it would be necessary to isolate most of the plutonium from the uranium before Pu^{+4} can be analyzed successfully. The isolation would take place using extraction, precipitation, or chromatographic methods.

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:

$$Th^{+4} + 2 \ NO_3^{-1} \rightarrow Th(NO_3)_2^{+2}$$
$$Ra^{+2} + EDTA^{-4 \, *} \rightarrow Ra(EDTA)^{-2}$$
$$U^{+4} + 5 \ CO_3^{-2} \rightarrow U(CO_3)_5^{-6}$$
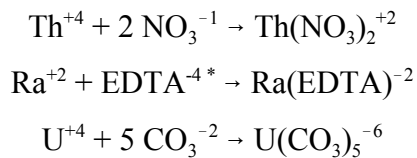
* $EDTA^{-4}$ = Ethylene diamine tetraacetate, $^{-1}(OOC)_2$-NH-CH_2-CH_2-NH-$(COO)_2^{-1}$

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:

$$Fe^{+2} + 6 \ H_2O \rightarrow Fe(H_2O)_6^{+2}$$
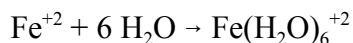
From an elementary standpoint, the process of complexation is simply the dynamic process of replacing one set of ligands, the solvent molecules, with another. The complexation of a metal ion in aqueous solution with a ligand, L, can be expressed as:

$$M(H_2O)_n^{+x} + L^{-y} \rightarrow M(H_2O)_{n-1}L^{x-y} + H_2O$$

Successive aquo groups can be replaced by other ligand groups until the complex ML_n^{x-ny} is formed as follows:

$$M(H_2O)_{n-1} L^{x-y} + L^{-y} \rightarrow M(H_2O)_{n-2} L_2^{x-2y} + H_2O, \text{ etc.}$$

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" (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 10 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.

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 lesser 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.

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, ethylene diamine, citrate
Tridentate	Diethylene triamine, 1,3,5 triaminocyclohexane
Polydentate	8-hydroxyquinoline, β-diketones (thenoyltrifluoroacetone [TTA]), ethylene diamine tetraacetic acid (EDTA), diethylene triamine pentaacetic acid (DTPA) Organophosphates: (octyl(phenyl)-*N,N*-diiso-butylcarbamoyl-methylphosphine oxide [CMPO]); tributylphosphate (TBP), trioctylphosphinic oxide (TOPO), quaternary amines (tricaprylyl-methylammonium chloride [Aliquat-336®]), triisooctylamine (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.

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, 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.
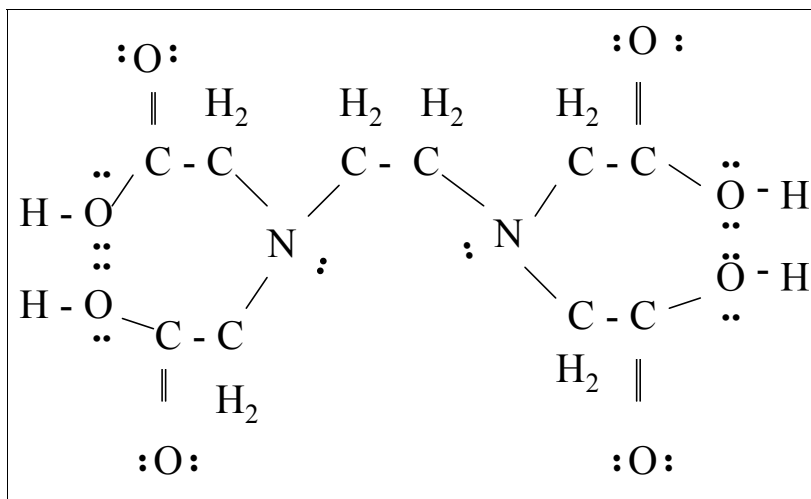
FIGURE 14.1 — Ethylene diamine tetraacetic acid (EDTA)

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 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 Ca^{+2}
and Mg^{+2} ions from hard water.

Various chelating agents bind more readily to certain cations, providing the specificity for separating ions by selective bonding. Occasionally, 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, $Ni(NH_3)^{+2}$.

Another class of ligands that is becoming increasingly important to the radiochemist doing laboratory analyses is the macrocyclic polyethers, commonly called crown ethers (Horwitz et al., 1991 and 1992a; Smith et al., 1996 and 1997). These compounds are cyclic ethers containing a number of regularly spaced oxygen atoms. Some examples are given in Figure 14.2.

[18]-crown-6   [12]-crown-4   dibenzo[18]-crown-6
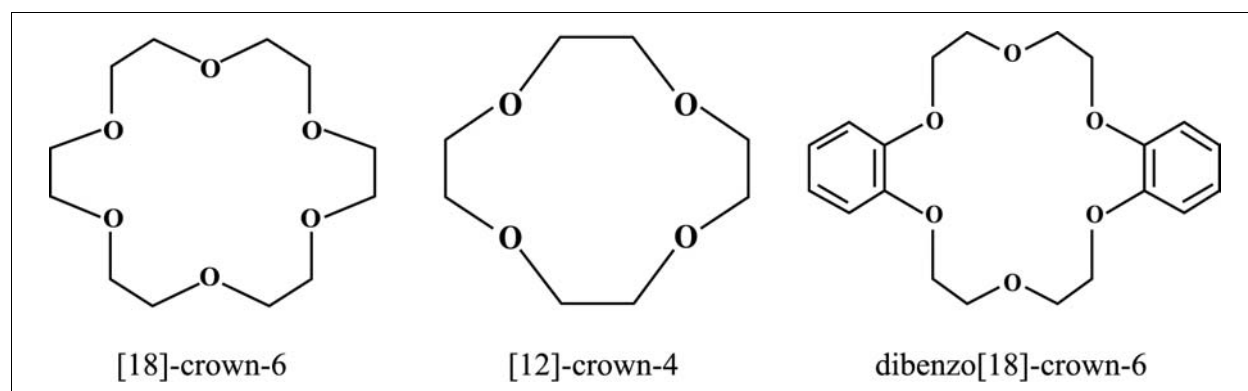
FIGURE 14.2 — Crown ethers

First identified in 1967, crown ethers have been shown to form particularly stable coordination complexes. The term, "crown ether," was suggested by the three-dimensional shape of the molecule. In the common names of the crown ethers, the ring size is given in brackets, and the number of oxygen atoms follows the word "crown."

Crown ethers have been shown to react rapidly and with high selectivity (Gokel, 1991; Hiraoka, 1992). This property is particularly significant when a separation requires high selectivity and efficiency in removing low-level species from complex and concentrated matrices, a situation frequently encountered in environmental or mixed-waste analyses. Because crown ethers are multidentate chelating ligands, they have very high formation constants. Moreover, because the metal ion must fit within the cavity, crown ethers demonstrate some selectivity for metal ions according to their size. Crown ethers can be designed to be very selective by changing the ring

size, the ring substituents, the ring number, the donor atom type, etc. For example, dibenzo-18-crown-6 forms a strong complex with potassium; weaker complexes with sodium, cesium, and rubidium; and no complex with lithium or ammonium, while 12-crown-4, with its smaller cavity, specifically complexes with lithium.

Other crown ethers are selective for radionuclide ions such as radium and UO_2^{+2}. Addition of 18-crown-6 to solutions containing NpO_2^{+2} causes the reduction of neptunium to Np(V) as NpO_2^{+1}, 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:

$$Th^{+4} + NO_3^{-1} \rightarrow Th(NO_3)^{+3}$$

$$Th(NO_3)^{+3} + NO_3^{-1} \rightarrow Th(NO_3)_2^{+2}$$
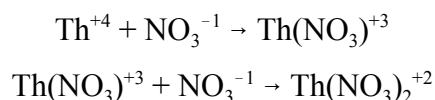
The final equation is:

$$Th^{+4} + 2NO_3^- \rightarrow Th(NO_3)_2^{+2}$$
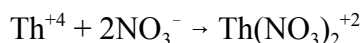
The stepwise formation (stability) constants are:

$$K_1 = \frac{[Th(NO_3)^{+3}]}{[Th^{+4}][NO_3^{-1}]}$$

and

$$K_2 = \frac{[Th(NO_3)_2^{+2}]}{[Th(NO_3)^{+3}][NO_3^{-1}]}$$

The overall formation (stability) constant is:

$$K_f = K_1 \cdot K_2 \frac{[Th(NO_3)_2^{+2}]}{[Th^{+4}][NO_3^{-1}]^2}$$

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).

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 $UO_2(CO_3)_3^{-4}$ increases the solubility of the uranium species in groundwater (Lindsay, 1988).

• Thorium (+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).

• Radium (+2) forms 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).

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.

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 $UO_2(CO_3)_3^{-4}$ complex ion after oxygen is used to convert U^{+4} to U(VI) (Grindler, 1962). 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). 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; Greenwood and Earnshaw, 1984).

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.

Thorium (+4) is bound more strongly to cation exchangers than most other cations (Hyde, 1960). The bound 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 exchange 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, 1997, 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). 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).

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, Sr^{+2} is separated from the bulk of the solution by direct precipitation of the sulfate, $SrSO_4$. The precipitate is redissolved by complexation with EDTA, $Sr(EDTA)^{-2}$, to separate it from lanthanides and actinides (DOE, 1997, 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).

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 Nb(V) ion in solution during several steps of the procedure (Kallmann, 1964). 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

Compleximetric 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). The soluble EDTA complex of thorium is the basis of a titrimetric determination of small amounts of thorium (Hyde, 1960).

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, $C_6H_5\text{-CO-CH}_2\text{-CO-C}_6H_5$ (Grindler, 1962).

14.4 Solvent Extraction

14.4.1 Extraction Principles

Solvent extraction has been an important separation technique 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, 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):

$$A_{aq} \rightleftharpoons A_{org}$$
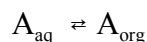
The solute can be in a solid or liquid form. The extracting solvent can be water, a water-miscible solvent, or a water-immiscible solvent; but it must be insoluble in the solvent of the liquid mixture. Solutes exhibit different solubilities in various solvents. Therefore, the choice of extracting solvent 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:

$$K_d = \frac{[A_{org}]}{[A_{aq}]}$$

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) 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 thermo-dynamically 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:

$$2A_{org} \rightleftharpoons (A)_{2, org}$$
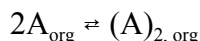
where the distribution ratio, D, is an alternate form of the distribution coefficient expressed by:

$$D = ([A_{org}]_{monomer} + [A_{org}]_{dimer})/[A_{aq}]$$

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:

$$D = K_d (1 + 2 K_2 [A_{org}])$$

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 techniques, 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). 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 considera-tions. 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) 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."

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 and thorium employs solvent extraction to separate the analytes before alpha counting (EPA, 1984). 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). 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).

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). 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:

$$RNH_2 + HCl \rightarrow RNH_3^{+1}Cl^{-1}$$
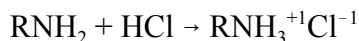
Correspondingly, carboxylic acids are converted to their carboxylates that are more soluble in water and less soluble in organic solvents. They are produced by treating the carboxylic acid with a base, such as sodium hydroxide:

$$RCOOH + NaOH \rightarrow RCOO^{-1}Na^{+1} + H_2O$$
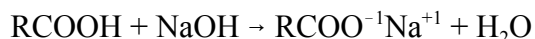
Multidentate organic anions that form chelates are important extracting agents. These reagents, such as the β-diketonates and thenoyltrifluoroacetone (TTA) (Ahrland, 1986), are commonly used for extracting the actinide elements. When the aqueous solution and organic phase come into contact with one another, 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 bis(2-ethylhexyl) phosphoric 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). However, the most widely used neutral extractants are the organophosphorus compounds such as TBP (tributylphosphate). The actinide elements thorium, uranium, neptunium, and plutonium easily form complexes with TBP (Choppin et al., 1995). 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).

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 tri-*n*-octylamine (TnOA) or 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.

TABLE **14.5 — Radioanalytical methods employing solvent extraction** [1]

Analyte	Extraction Conditions (Reference)
$^{89/90}Sr$	From soils and sediments with dicyclohexano-18-crown-6 in trichloromethane with back extraction with EDTA (Pimpl, 1995)
$^{99}TcO_4^-$	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 methyl ethyl ketone (Paducah R-46); from alkaline nuclear-waste media with crown ethers (Bonnesen et al., 1995)
^{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)
Radium through Californium	From soil following KF-pyrosulfate fusion and concentration by barium sulfate precipitation with Aliquat-336® in xylene (Sill et al., 1974)
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)
Thorium	From aqueous samples after ion exchange with TTA, TIOA, or Aliquat-336® (DOE, 1997, Method RP570)
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)

(1) This list is representative of the methods found in the literature. It is not an exhaustive compilation, nor does it imply preference over methods not listed.

14.4.5 Solid-Phase Extraction

A technique closely related to solvent extraction is solid-phase extraction (SPE). SPE is a solvent-extraction system in which one of the phases is made stationary by adsorption onto 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 Technologies, Inc., Darien, IL) (Dietz and Horwitz, 1993; Horwitz et al., 1991, 1992a, 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 is the use of fibrous discs impregnated with high-molecular-weight chelates that select for certain elements such as Cs, Sr, and Tc (Empore Discs, 3M Company, and the TEVA® Disc, Eichrom Technologies, 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	dimethylglyoxime	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 1992a); Water (ASTM, D5811-95; DOE, 1997, 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, 1997, Method RP550)
Pb-210	4,4'(5')-bis(t-butyl-cyclohexano)-18-crown-6 in isodecanol	Water (DOE, 1997, Method RP280); Geological materials (Horwitz et al., 1994; Woittiez and Kroon, 1995); complex metal ores (Gale, 1996)
Ra-228	CMPO in tributyl phosphate or HDEHP impregnated in Amberlite XAD-7	Natural waters (Burnett et al., 1995); Volcanic rocks (Chabaux, 1994)

Analyte	Ligand	Method Citations
Rare earths	diamyl,amylphosphonate	Actinide-containing matrices (Carney, 1995)
	CMPO in tributyl phosphate and HDEHP impregnated in Amberlite XAD-7	Sequential separation of light rare earths, U, and Th in geological materials (Pin et al., 1996)
	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	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., 1992b)
	tri-*n*-octylphosphine oxide [TOPO] and 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 et al., 1997; Smith et al., 1996 and 1997).

These SPE membranes significantly reduce extraction time and reagent use in the processing of large environmental water samples. Samples typically are processed through the membranes at flow rates of at least 50 mL/min; a 1 L 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 of Liquid-Liquid Solvent Extraction

• 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. This also provides significant pre-analysis concentration of the analyte.

• 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.

14.4.6.2   Disadvantages of Liquid-Liquid Solvent Extraction

• Cumbersome for a large number of samples or for large samples.

• Often requires toxic 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 with the phase-separation process.

• 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.

14.4.6.3   Advantages of Solid-Phase Extraction Media

• Column/filter extraction may be unattended.

• Column/filter extraction is very selective.

- Generates a low volume of waste, can often be applied to samples dissolved in very acidic media.

- Requires relatively inexpensive equipment.

- In may cases can be correlated with liquid/liquid extraction.

14.4.6.4   Disadvantages of Solid-Phase Extraction Media

- Extraction columns cannot be reused—a cost factor.

- Any suspended matter may be filtered by the media, carrying contaminants into the next step of the separation or analysis.

- Flow rate through columns are generally slow (1-3 mL/min).

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), 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). A list of the elements that can be separated by volatilization and their chemical form(s) upon separation are given in Table 14.7.

TABLE 14.7 — Elements separable by volatilization as certain species

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
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 (a)	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)	Sn (bd)	Sb (bd)	Te (bcd)	I (abd)	Xe (ad)
Cs (a)	Ba (a)	La*	Hf (d)	Ta (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**															

La*	Ce*	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Ac**	Th** (d)	Pa (d)	U (d)	Np (d)	Pu	Am	Cm	Bk	Cf	Es	Fm	Mv	No	

Key to volatile form of element: a - Element; b - Hydride; c - Oxide; c^* - Permanganic acid; c^+ - Boric acid; d - Halides; d^* - Chromyl chloride

(From Coomber, 1975)

McMillan (1975) states:

> "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):

> "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
> 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). Korkisch (1969) states: "Nevertheless, some of the elements of interest to radiochemists can be very effectively separated by distillation as their volatile chlorides, bromides, and oxides .... [T]hese elements are germanium (Ge), selenium (Se), technetium (Tc), rhenium (Re), ruthenium (Ru), and osmium (Os)." (Also see DOE, 1997, 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). Distillation procedures are discussed for many inorganic applications in Dean (1995) and for less common radioanalytes in DeVoe (1962) and 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; DOE, 1997). 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 (^{3}H), 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 used for smaller samples (DOE, 1997, 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 is separated from aqueous samples by distillation from acidic solutions into alkaline

solutions (EPA, 1973). 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, 1997, 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). Metals are sometimes distilled in their elemental form—polonium in bismuth or lead (McMillan, 1975).

Radium-226 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. Because 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-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," 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). 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). 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 Section 14.9.3.7, "Oxidation and Reduction," 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). 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).

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). 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). 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). 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).

14.6.2 Separation of Radionuclides

Although electrodeposition is not frequently used as a radiochemical separation technique, several radionuclides [including iron (Hahn, 1945), cadmium (Wright, 1947), and technetium (Flagg, 1945)] have been isolated by electrodeposition on a metal electrode. Electrodeposition is, however, the standard separation technique for polonium, copper, and platinum. Polonium is isolated through deposition on nickel from a strong hydrochloric acid (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). Numerous metals have been deposited on thin metal films by electrolysis with a magnesium cathode. According to Coomber, "Electrodeposition of metals can be sensitive to the presence of other substances" (Coomber, 1975). Deposition of polonium on silver 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. "In many cases the uncertainties of yield can be corrected by the use of another radioisotope as an internal standard" (Coomber, 1975).

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 electro-deposition 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 it should be assessed when electrodeposition is being considered. Also see Section 14.8.4, "Coprecipitation."

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.

- Takes longer than microprecipitation, because it requires evaporation of solutions after column separation and ashing to remove all organic residue.

- Subject to interference from such metals as Fe or Ti.

- Subject to interference from such ions as fluoride.

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 or helium, 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). 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).

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 using paper and thin-layer chromatography. Modified and treated papers have been used to separate the various valence states of technetium (Coomber, 1975).

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 the 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:

$$K_d = \frac{[C_1 / g_{resin}]}{[C_2 / mL_{solution}]}$$

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:

$$\text{Separation factor } (\alpha) = \frac{[K_{d,a}]}{[K_{d,b}]}$$

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 other cation (e.g., Na^{+1}, Ca^{+2}, Al^{+3}, 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:

$$R_{esin}SO_3^{-1}H^{+1} + Cs^{+1} \rightarrow R_{esin}SO_3^{-1}Cs^{+1} + H^{+1}$$
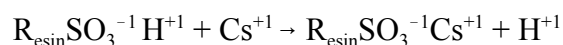
Diffusion is an important process during ion exchange; the solute ions must penetrate the pores of the spherical resin beads to exchange with the existing ions. Equilibrium is established between each ion in the analyte solution and the exchange site on the resin. The ion least tightly bonded to the 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 for group 1 cations 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 effec-tively 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 (400 – 50 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.

• Nonionic 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 (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. Other functional groups can be used for specific purposes.

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), or converted to an anionic complex with citrate or EDTA and separated on a quaternary ammonium polystyrene resin (Sedlet, 1966).

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). Thorium cations (Th^{+4}) form anionic nitrate complexes that bind to an anion-exchange resin containing the quaternary complex, $R-CH_2-N(CH_3)_3^{+1}$. 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.

TABLE 14.9 — **Common ion-exchange resins** [*]

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.
Cation-exchange resins - gel type - strongly acidic - sulfonic acid functionality			

Resin type & nominal % cross-link	Minimum wet capacity meq • mL⁻¹	Density (nominal) g • mL⁻¹	Description
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 exchanges larger alkali-metal ions from smaller alkali-metal ions, particularly cesium.

* 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.

The behavior of the elements on anion- and cation-exchange resins is summarized for several resins in Faris and Buchanan (1964), Kraus and Nelson (1956), and Nelson et al. (1964). The behavior in concentrated HCl is illustrated for cations on cation-exchange resins in Figure 14.3 (Dorfner, 1972) and for anions on anion-exchange resins in Figure 14.4 (Dorfner, 1972).
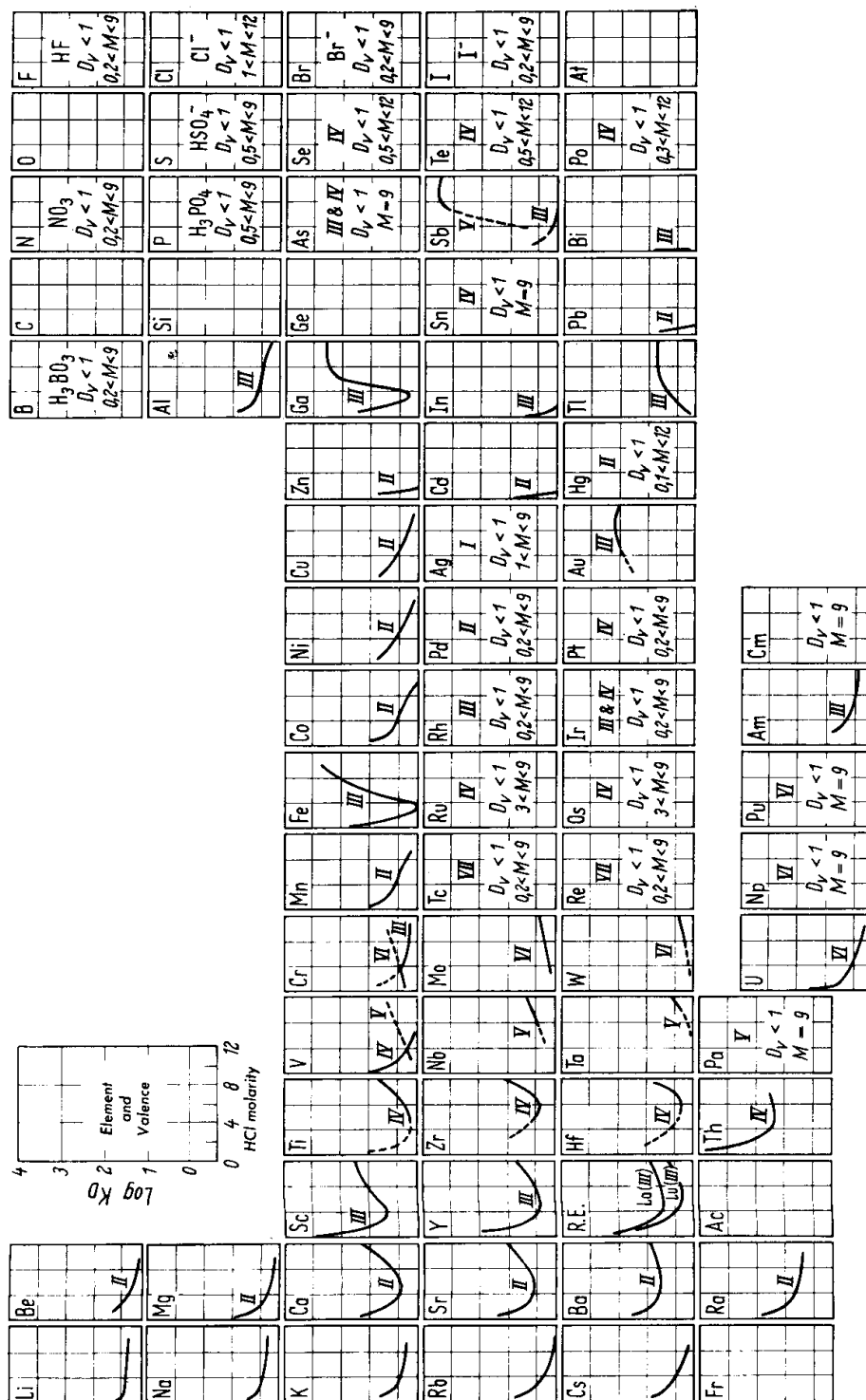
FIGURE 14.3 — The behavior of elements in concentrated hydrochloric acid on cation-exchange resins
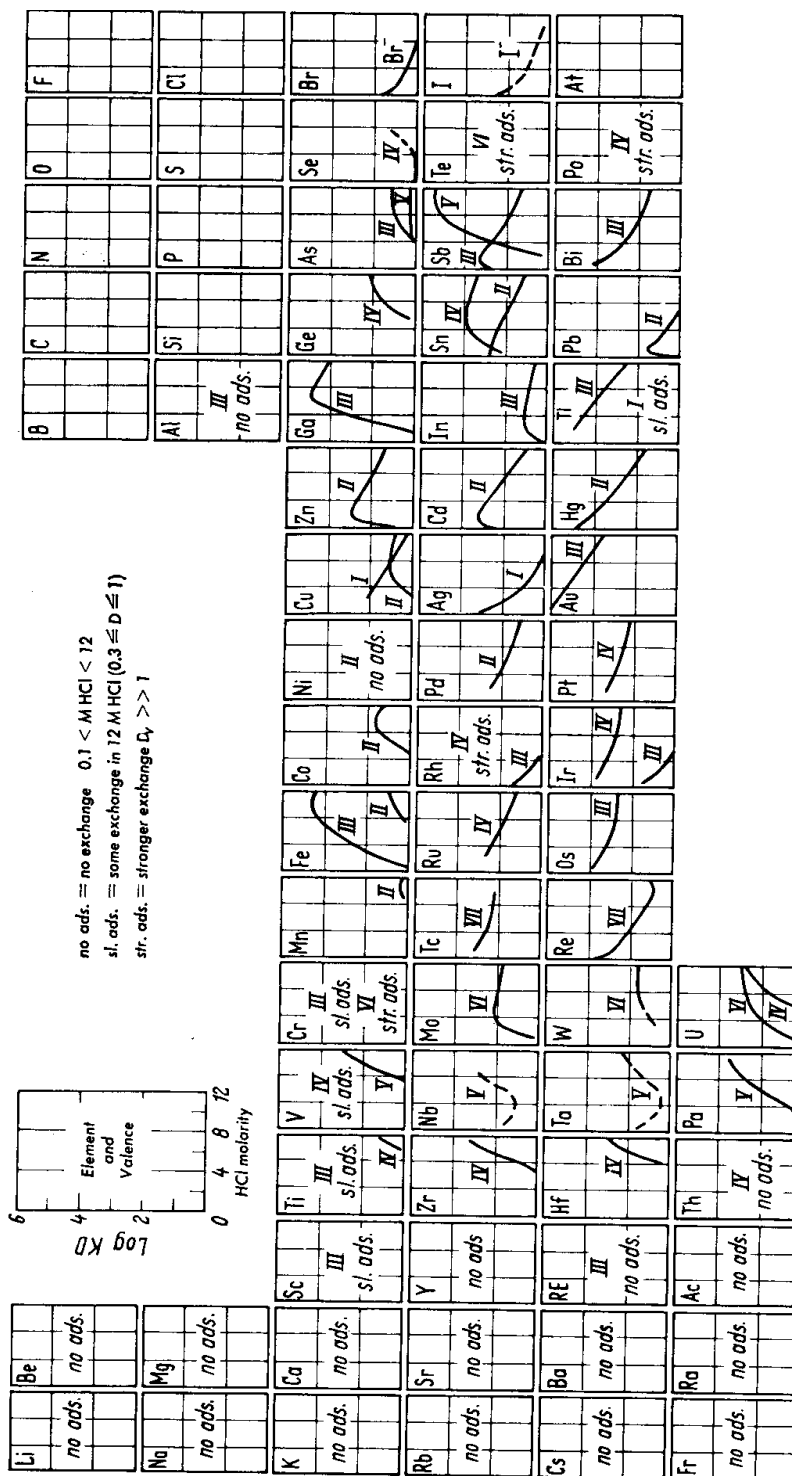
Figure 14.4 —The behavior of elements in concentrated hydrochloric acid on anion-exchange resins

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 Sr^{+2} and 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 $^{89/90}$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 (1.657×10^{-20} g). 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).

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 almost 14 MPa). 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).

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 or nitrogen—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.

14.7.8.1   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.

14.7.8.2   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 radio-analytical 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}
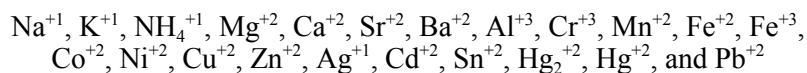
There are general rules of solubilities for the common cations found in most basic chemistry texts (e.g., Pauling, 1970).

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 trivalent 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).

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.

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

Chemists routinely face challenges in the laboratory as a result of the phenomenon of solubility. Examples include keeping a dissolved component in solution and coprecipitating a trace-level analyte from solution.

Solubility equilibrium refers to the equilibrium that describes a solid (s) dissolving in solution (soln), such as strontium carbonate dissolving in water, for example:

$$SrCO_3(s) \rightleftharpoons Sr^{+2} \text{ (soln)} + CO_3^{-2} \text{ (soln)}$$
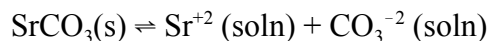
or, alternately, a solid forming from solution, with the carbonate precipitating:

$$Sr^{+2} \text{ (soln)} + CO_3^{-2} \text{ (soln)} \rightarrow SrCO_3\downarrow \text{ (s)}$$
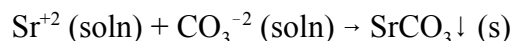
The solubility product constant, K_{sp}, is the equilibrium constant for the former process, a solid dissolving and forming ions in solution. Leussing (1959) explains K_{sp} in general terms:

"For an electrolyte, $M_m N_n$, which dissolves and dissociates according to the equation:

$$M_m N_n(s) \leftrightharpoons M_m N_n(soln) \leftrightharpoons mM^{+n}(soln.) + nN^{-m}(soln)$$
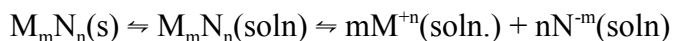
"The equilibrium conditions exists that:

$$a_{MmNn(s)} = a_{MmNn(soln)} = a^m{}_{M+n(soln)} \cdot a^n{}_{N-m(soln.)}$$

"[The value *a* is the *activity* of the ions in solution, a measure of the molar concentration (moles/L) of an ion in solution under ideal conditions of infinite dilution.] (Also see Section 14.6.1, "Principles of Electrodeposition," for a discussion of activity as applied to the Nernst equation.) [This equation] results in the familiar solubility product expression since the activity of a solid under given conditions is a constant. 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 $\gamma \leq 1$], [this] equation becomes...

$$[M^{+n}]^m [N^{-m}]^n \gamma^m{}_{M+n} \gamma^n{}_{N-m} = a \text{ constant} = K_{sp} \text{''}$$

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 $(1 \times 10^{-6}) \times (0.0016) = 1.6 \times 10^{-9}$.

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). 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 complete reaction. Practical radiochemical separations performed based on solubility (either K_{sp} or coprecipitation phenomenon) are best described by Salutsky (1959).

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:

$$PbCl_2(s) \rightleftharpoons Pb^{+2}(soln) + 2\ Cl^-(soln)$$
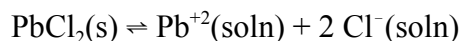
"After the two solutions are mixed, $[Pb^{+2}] = 1.3 \times 10^{-2}$ M (0.2 L $\times$ 2.0×10^{-2} M/0.3 L), and $[Cl^-] = 1.7 \times 10^{-3}$ M (0.1 L $\times$ 5.0×10^{-3} M/0.3 L). The value for the ion product is calculated from the expression

$$Q = [Pb^{+2}]\ [Cl^-]^2 \text{ or } [1.3 \times 10^{-2}]\ [1.7 \times 10^{-3}]^2$$

$$Q = 3.8 \times 10^{-8}$$

"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:

$$Na_2CO_3(s) \rightleftharpoons 2\ Na^{+1}(soln) + CO_3^{-2}(soln)$$

$$SrCO_3(s) \rightleftharpoons Sr^{+2}(soln) + CO_3^{-2}(soln)$$
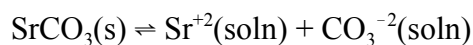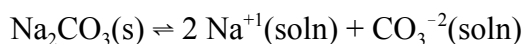
Alternatively, if a complexing agent or ligand is available that can react with the cation of a precipitate, the solubility of the compound can be markedly enhanced. An example from Section 14.3.4.3, "Formation and Dissolution of Precipitates," provides an illustration of this phenomenon. In the determination 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, 1997, Method RP520):

$$SrSO_4(s) \rightarrow Sr^{+2}(soln) + SO_4^{-2}(soln)$$

$$Sr^{+2}(soln) + EDTA^{-4} \rightarrow Sr(EDTA)^{-2}(soln)$$
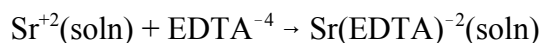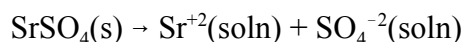
Additionally, many metal ions are weakly acidic and hydrolyze in solution. Hydrolysis of the ferric ion (Fe^{+3}) is a classical example of this phenomenon:

$$Fe^{+3} + H_2O \rightarrow Fe(OH)^{+2} + H^{+1}$$
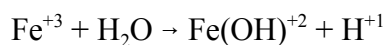
When these metal ions hydrolyze, producing a less soluble complex, the solubility of the salt is a function of the pH of the solution, increasing as the pH decreases. The minimum solubility is found under acidic conditions when the concentrations of the hydrolyzed species become negligible. As demonstrated 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):

- 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. It has been demonstrated that the solubility of smaller particles is greater than that of larger particles of the same material.

- 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$_2$O$_4$) can exchange with either sulfate or barium ions:

$$CaC_2O_4(s) + SO_4^{-2}(soln) \rightarrow CaSO_4(s) + C_2O_4^{-2}(soln)$$

$$CaC_2O_4(s) + Ba^{+2}(soln) \rightarrow BaC_2O_4(s) + Ca^{+2}(soln)$$
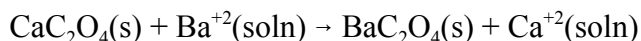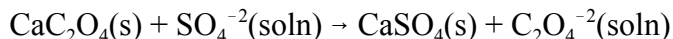
The excess of common ions that appears on the right-hand side of the equations represses the solubility of calcium oxalate according to the laws of mass action.

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):

"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) and Salutsky (1959), 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).

- *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* on page 14-68). Digestion is used in an ^{131}I determination to increase the purity of the lead iodide (PbI$_2$) crystals (EPA, 1984).

- *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$_3$OH)-water mixture and can be effectively precipitated from the solution (Berg, 1963). 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:

$$Ca^{+2} + C_2O_4^{-2} \rightarrow CaC_2O_4$$
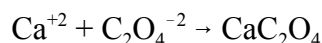
Because the oxalate concentration is affected by the hydrogen-ion concentration,

$$H^{+1} + C_2O_4^{-2} \rightarrow HC_2O_4^{-1},$$
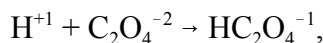
increasing the hydrogen-ion concentration (lowering the pH) decreases the oxalate ion concentration by forming bioxalate, which makes the precipitate more soluble. Therefore, decreasing the hydrogen-ion concentration (raising the pH), therefore, aids precipitation. Similar effects are obtained with carbonate precipitates:

$$Sr^{+2} + CO_3^{-2} \rightarrow SrCO_3$$

$$H^{+1} + CO_3^{-2} \rightarrow HCO_3^{-1}$$
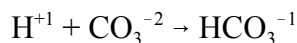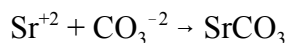
Many metal sulfides are formed in a solution of hydrogen sulfide by generating the sulfide ion (S^{-2}) at suitable pH:

$$H_2S \rightarrow H^{+1} + HS^{-1}$$

$$HS^{-1} \rightarrow H^{+1} + S^{-2}$$

$$Pb^{+2} + S^{-2} \rightarrow PbS$$
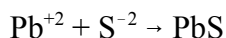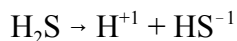
The pH can also influence selective formation of precipitates. Barium chromate will

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).

- *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) 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). Other agents alter the pH of the solution (see "*pH Effect*" on the previous page). Hydrolysis of urea, for example, produces ammonia, which raises the pH of a solution:

$$H_2NCONH_2 + H_2O \rightarrow CO_2 + 2\ NH_3$$
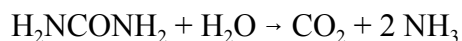
**TABLE 14.11 — Summary of methods for utilizing precipitation
from homogeneous solution**

Precipitant	Reagent	Element Precipitated
Hydroxide	Urea	Al, Ga, Th, Fe^{+3}, Sn, and Zr
	Acetamide	Ti
	Hexamethylenetetraamine	Th
	Metal chelate and H$_2$O$_2$	Fe^{+3}
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^{+3}
	Ce^{+3} and bromate	Ce^{+4}
Carbonate	Trichloroacetate	Rare earths, Ba, and Ra
Chromate	Urea and dichromate	Ba and Ra
	Potassium cyanate and dichromate	Ba, Ra
	Cr^{+3} and bromate	Pb
Periodate	Acetamide	Pb
Chloride	Silver ammonia complex and ß-hydroxyethyl acetate	Ag
Arsenate	Arsenite and nitrite	Zr
Tetrachlorophthalate	Tetrachlorophthalic acid	Th
Dimethylglyoxime	Urea and metal chelate	Ni
8-Hydroxyquinoline	Urea and metal chelate	Al
Fluoride	Fluoroboric acid	La

Source: Salutsky, 1959.

- *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 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**

Condition	Form of Impurity*			
	Mixed Crystals	**Surface Adsorption**	**Occlusion and Inclusion**	**Post-precipitation**
Dilute solutions	○	+	+	○
Slow precipitation	+	+	+	-
Prolonged digestion	-	+	+	-
High temperature	-	+	+	-
Agitation	+	+	+	○
Washing the precipitate	○	+	○	○
Reprecipitation	+	+	+	○

*Symbols: +, increased purity; -, decreased purity; ○, little or no change in purity
Source: Salutsky, 1959.

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, $BaSO_4$ (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 example, to determine ^{90}Sr in environmental samples, stable strontium (containing no radioisotopes of strontium) is added to increase the concentration of total strontium to the point that the common ion effect causes precipitation. 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, 1997, 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) 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). 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). 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 and hafnium as phosphates are examples of this broader definition (Salutsky, 1959). 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). 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):

$$\log(I_i/I_f) = \lambda \log(P_i/P_f)$$

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). 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 the process for a specific ion. 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). 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).

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):

$$(I/P)_{ppt.} = D (I/P)_{soln.}$$

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). According to Hermann and Suttle (1961):

> "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."

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).

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 (1959):

> "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."

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). 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).

"Because adsorption is a surface phenomenon, the larger the surface area of a precipitate, the greater the adsorption of impurities" (Salutsky, 1959). 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). 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)."

Adsorption also depends on the concentration of an ion in solution (Berg, 1963). A high concentration of impurity increases the probability of solute interaction at the solid surface and favors adsorption. Salutsky (1959) 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."

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). 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). 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). 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 accomp-
lished 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). Wahl and Bonner
(1951) 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)."

Considering the principles of precipitation and coprecipitation, radium is coprecipitated quantita-
tively 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 crystal-
line 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 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). 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 carriers 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 (Hermann and Suttle, 1961).

> "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."

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	+3	hydroxide iodate fluoride, oxalate, phosphate, hydroxide oxalate acetate fluoride, sulfate acetate	Am^{+3}, Fe^{+3} Ce^{+4}, Th^{+4}, Zr^{+4} La^{+3}, Ce^{+3}, Nd^{+3}, Bi^{+3} Ca^{+2} Am^{+4} La^{+3} UO_2^{+2}	
Cs	+1	phosphomolybdate, chloroplatinate, bismuth nitrate, silicomolybdate	Cs^{+1}	
Co	+2	hydroxide potassium cobalt nitrate 1-nitroso-2-napthol sulfide	Co^{+2} Co^{+2} Co^{+2} Co^{+2}	
Fe	+3	hydroxide ammonium pyrouranate	Fe^{+3} Fe^{+3}	
I	−1	iodide	Pb^{+2}, Ag^{+1}, Pd^{+2}, Cu^{+2}	
Ni	+2	dimethylglyoxime hydroxide	Ni^{+2}	
Nb	(V)	hydroxide, phosphate	Nb(V)	
Np	+4	phosphate	Ca^{+2}	
Po	+4	tellurium tellurate selenium dioxide hydroxide sulfide	Te Pb^{+2} Se or Se^{-2} Mn^{+4} Fe^{+3}, Al^{+3}, La^{+3} Cu^{+2}, Bi^{+2}, Pb^{+2}	Tellurate reduced with $SnCl_2$
Pu	+3 +4 (VI)	fluoride sulfate fluoride oxalate, iodate phosphate sodium uranylacetate	La^{+3}, Nd^{+3}, Ce^{+3}, Ca^{+2} $La^{+3}(K^{+1})$ La^{+3}, Nd^{+3}, Ce^{+3} Th^{+4} Zr^{+2}, Bi^{+3} UO_2^{+2}	

Radionuclide	Oxidation State	Coprecipitate	Carrier[2]	Notes
Ra	+2	hydroxide sulfate, chromate, chloride, bromide oxalate, phosphate fluoride	Fe^{+3} Ba^{+2} Th^{+4}, Ca^{+2}, Ba^{+2} La^{+3}	
Sr	+2	carbonate nitrate chromate sulfate phosphate hydroxide	Sr^{+2}, Ba^{+2}, Ca^{+2} Sr^{+2}, Ba^{+2} Ba^{+2} Sr^{+2}, Ca^{+2}, Pb^{+2} Sr^{+2} Fe^{+3}	Alkaline pH
Tc	+4 (VII)	hydroxide chlorate, iodate, perruthenate, tetrafluoroborate sulfide	Tc^{+4}, Fe^{+3}, Mn^{+2} $(Phenyl)_4As^{+1}$ Tc^{+7}, Re^{+7}, Cu^{+2}, Cd^{+2}	
Th	+4	hydroxide fluoride iodate phosphate, peroxide sulfate oxalate	Th^{+4}, La^{+3}, Fe^{+3}, Zr^{+3}, Ac^{+3}, Zn^{+2} Th^{+4}, La^{+3}, Nd^{+3}, Ce^{+3} Th^{+4}, Zr^{+3} Th^{+4}, Bi^{+3} Ba^{+2} Ca^{+2}	
U	+4	cupferron, pyrophosphate, phosphate, iodate, sulfate, oxalate	U^{+4}	
		fluoride	La^{+3}, Nd^{+3}	
	(V)	phosphate	Zr^{+3}	
		sulfate	Ca^{+2}	
	(VI)	cupferron	U(VI)	Neutral solution
		pyrouranate	U(VI)	From aqueous NH_3, many ions stay in solution as NH_3 complex
		phosphate	U(VI), Al^{+3}	
		peroxide	U(VI)	Th^{+4}, Zr^{+3} also coprecipitate
		hydroxide	Fe^{+3}	Without carbonate
		fluoride	Th^{+4}	
Zr	+4	hydroxide	Fe^{+3}	

(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 as the carrier, a different isotope would be used to assess recovery.

TABLE 14.14 — Coprecipitation behavior of plutonium and neptunium

Carrier Compound	Pu^{+3}	Pu^{+4}	Pu(VI)	Np^{+4}	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^{+4} hypophosphate		C	NC			
Oxalates:						
Lanthanum oxalate	C	C	NC	NC		
Bismuth oxalate	C	C	NC			
Thorium oxalate	C	C	NC	C		
U^{+4} 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). 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). 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.
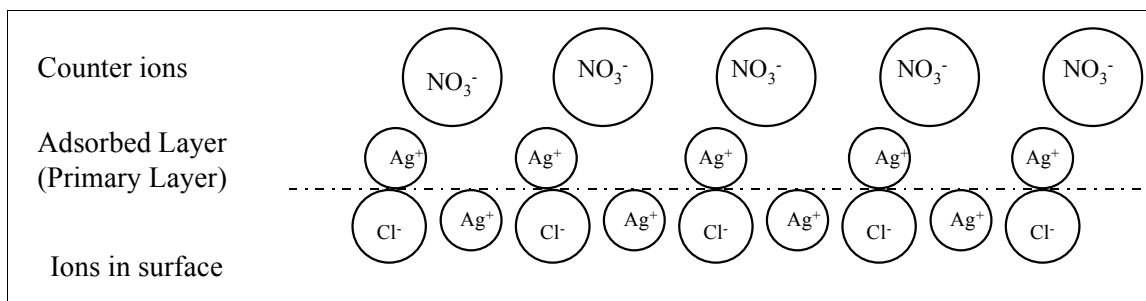
FIGURE 14.5 — The electrical double layer: A schematic representation of adsorption of nitrate counter-ions onto a primary adsorbed layer of silver ions at the surface of a silver chloride crystal (Peters et al., 1974).

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* on page 14-72).

- 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):

- 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). 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 $[Zr(IO_3)_4]$ precipitation to remove impurities (with Ce^{+3} staying in solution), and reoxidation to Ce^{+4}.

14.8.6 Separation of Precipitates

The process of precipitation chemically separates an analyte from contaminants or other analytes. Precipitation generally is followed by one of two techniques that physically separates the precipitate: centrifugation or filtration.

Centrifugation is a technique that can be used for precipitates of many different physical forms. The best way to demonstrate the utility of centrifugation in radiochemical analyses is by example:

Example of Centrifugation

A method of radium analysis coprecipitates radium with barium using sulfuric acid to isolate the radium from its progeny. When the precipitation is completed, the mixture is centrifuged. The supernatant solution contains contaminants and radium progeny and is decanted. The precipitate is washed, *in situ*, with an isotonic sulfuric acid solution to maintain the insolubility of the precipitate, and to further enhance the removal of the contaminants. The mixture is re-centrifuged and the supernate again decanted.

This example demonstrates that centrifugation separates and purifies the precipitate without disturbing the mechanical flow of the separation process, and it minimizes the introduction of new contaminants by using the same glassware. It is noteworthy that there are several instances of using centrifugation to discard the precipitate and retain the supernate (e.g., the separation of barium from strontium using chromate). Separation by filtration at this point (not the final analytical step) would involve transfer onto and subsequent removal from the filter media. Filtration would be time consuming and risk low yield for the analysis. The speed and capacity of the centrifuge is dictated by the type of precipitate (e.g., gelatinous, crystalline, amorphous etc.), the sample size being processed, and the ancillary procedural steps to purify the precipitate.

The final separation of the analyte immediately preceding counting techniques is generally best suited by using filtration techniques. 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):

- 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).

- 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.

14.8.7 Advantages and Disadvantages of Precipitation and Coprecipitation

14.8.7.1   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).
- Not energy- or resource-intensive compared to other techniques (e.g., solvent extraction).

14.8.7.2   Disadvantages

- Can be time consuming to digest, filter, or wash the precipitate.
- Precipitate can be contaminated by carrying of ions or postprecipitation.
- Large 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 to be determined easily, even though the number of atoms (and mass percent) of these materials is vanishingly small. Table 14.15 identifies the number of atoms and mass present in several radionuclides, based on an activity of 500 dpm (8.33 Bq).

TABLE 14.15 — **Atoms and mass of select radionuclides equivalent to 500 dpm**

Radionuclide	Half-life[*]	Number of Atoms	Mass (g)
Radium-226	1,600 y	6.0×10^{11}	2.3×10^{-10}
Polonium-210	138.3 d	1.5×10^{8}	5.0×10^{-14}
Lead-212	10.6 h	4.5×10^{5}	1.6×10^{-16}
Thallium-208	3.1 min	2.3×10^{3}	8.0×10^{-19}

[*] Half-lives taken from Brookhaven National Laboratory, National Nuclear Science Database (www.nndc.bnl.gov/).

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 nonradioactive 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 because $AgIO_3$ 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, because 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

Nonisotopic 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). 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, nonisotopic 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^{+4} and Pu^{+4} in their final separation as insoluble fluorides by the process of coprecipitation (Metz and Waterbury, 1962) (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 (VI) form will not. Uranium(VI) 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. Because uranium and lanthanum are not chemically equivalent, the laws of solubility product constant for lanthanum cannot be applied to uranium. For these types of processes, separate methods, usually involving a tracer isotope of the analyte, should be used to determine the chemical yield of the process.

For alpha counting, rare-earth fluorides (such as NdF_3) are frequently used to coprecipitate the transuranic elements (Hindman, 1983 and 1986; Sill and Williams, 1981).

Another group of nonisotopic 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. Radioisotopes of Sr^{+2} and Ba^{+2} will coprecipitate with ferric hydroxide [$Fe(OH)_3$], while 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 ($SrSO_4$ or $CaSO_4$), 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 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, Ra coprecipitates with all Ba compounds and, to a lesser extent, with most Sr and Pb 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 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 radioisotopes of the 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 Ba and 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 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 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 to 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. Cesium(+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, zirconium, niobium, hafnium, and titanium. 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 to 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(+4) 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 to 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 $Zr(IO_3)_4$], cesium and thorium oxalates [$Th(C_2O_4)_2$], barium sulfate, zirconium phosphate [$Zr_3(PO_4)_4$], 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 and neptunium 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 radio-nuclides 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).

14.9.2.5   Yield of Isotopic Carriers

The use of an isotopic carrier to determine the chemical yield (recovery) 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, nonhygroscopic, etc.

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:

$$\text{Percent Yield} = \left[\frac{\text{mass of carrier in final separation step}}{\text{mass of carrier added}} \right] \times 100$$

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, ultra-violet/visible spectrometry, titrimetry, and potentiometry.

14.9.3 Tracers

The term "tracer"was used classically to express the concentration of any pure radionuclide in solution that had a mass too small to be measured by an analytical balance ($<10^{-5}$ to 10^{-6} 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. Americium-243 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 nonisotopic 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).

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. Plutonium-236 is used as a tracer for $^{239/240}$Pu analysis, for example. Plutonium-236 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, "Analysis of Specific Radionuclides"). 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:

- Strontium-85 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.

- Technetium-99m, 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.

- Europium-152 and ^{145}Sm are frequently used in the development of a new method to estimate the behavior of the +3 actinides and lanthanides.

- Tritium, ^{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.

- Thorium-229 is used for Th determinations, both in alpha spectroscopy and inductively

coupled plasma-mass spectroscopy (ICP-MS).

- Uranium-232 is commonly used as a tracer in alpha spectroscopy, whereas ^{233}U is used commonly for ICP-MS determinations. It should be noted that ^{232}U decays to ^{228}Th and therefore this needs to be taken into account when determining other alpha emitters.

- Plutonium-242 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.

- Americium-243 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):

$$m \cdot UO_2^{+2} + p \cdot H_2O \rightarrow (UO_2)_m(OH)_p^{2m-p} + p \cdot H^{+1}$$
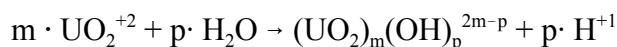
At tracer quantities, the equilibrium will shift to the left as the amount of the uranyl ion decreases. At 10^{-3} molar (pH 6), the uranyl ion is 50 percent polymerized; at 10^{-6} molar, there is negligible polymerization.

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). Adsorption depends on (see *Surface Adsorption* on page 14-72):

- *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 uncertainty that would go undetected at normal concentrations.

However, the adsorption process has been shown to be useful in some instances. For example, carrier-free 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 Nb has been adsorbed on glass fiber filters for a fast specific separation technique (Friedlander et al., 1981).

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 14.8.4).

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). 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), onto ion-exchange resins, followed by selective elution, has been developed into a very efficient separation technique (Wahl and Bonner, 1951) (see Section 14.7.4, "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 ...The transuranium elements in the solution were ... separated from one another by elution ... through a cation-exchange column."

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). Carrier-free tracers can become colloidal by two mechanisms:

1. Sorption onto a preexisting colloidal impurity (approximately 0.001 to 0.5 µm), such as dust, cellulose fibers, glass fragments, organic material, and polymeric metal hydrolysis products (Adolff and Guillaumont, 1993; Choppin et al., 1995).

2. Polycondensation of a monomeric species consisting of aggregates of 10^3 to 10^7 radioactive atoms (Adolff and Guillaumont, 1993).

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):

• 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):

• *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. Ultrapure water prepared with micropore filters reduces the amount of foreign particles. However, the preparation of water that is completely free of suspended particles is difficult.

- *Electrolytes.* Electrolytes affect the nature (species) of the tracer ions in solution (see Section 14.10, "Analysis of Specific Radionuclides"), 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). 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):

- 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 detectable 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).

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). 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 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). 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). 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:

$$PuO_2^{+2} + 4\ H^{+1} + Hg \rightarrow Pu^{+4} + Hg^{+2} + 2\ H_2O$$
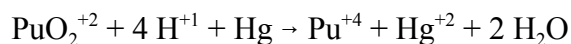
the Nernst equation is used to calculate the redox potential, E, from the standard potential, E^0:

$$E = E^0 - kT\ \ln([Pu^{+4}][Hg^{+2}]/[PuO_2^{+2}][H^{+1}]^4)$$

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) or other substance, leaving the impurities in solution (Friedlander et al., 1981). The selectivity and efficiency, characteristic of deposition of macroquantities 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 alpha, beta, or proportional counting measurements (Wahl and Bonner, 1951).

Deposition by electrochemical displacement is sometimes used for the separation of tracer from bulk impurities (Friedlander et al., 1981). 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, Table 6F) contains electrochemical methods used for the oxidation and reduction of carrier-free tracers.

14.10 Analysis of Specific Radionuclides

14.10.1   Basic Principles of Chemical 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.

It is important to note that "chemical equilibrium" and "radioactive equilibrium" are two distinct phenomena that come together when performing chemical separations of radionuclides. See Attachment 14A at the end of this chapter for a thorough discussion of the phenomenon of "radioactive equilibrium."

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 $^{89/90}$Sr; EPA, 1980, Method 905.0).

- A stable isotope tracer (i.e., enriched ^{18}O, ^{15}N, and ^{13}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 a radioactive strontium isotope (i.e., ^{85}Sr) could be added and determined by the method appropriate for that analysis.

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) 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:

$$^{212}Pb(NO_3)_2(s) + PbCl_2(s) \rightarrow Pb(NO_3)_2 + {}^{212}PbCl_2$$
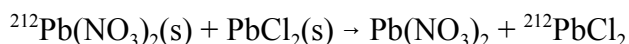
Any of the following techniques may be employed to achieve both chemical and isotopic equilibration:

- 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 (1971) summarize the introduction to equilibration (isotopic exchange):

"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 (^{3}H), 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) 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):

$$Ra^{+2} + x \cdot H_2O \rightarrow Ra(H_2O)_x^{+2}$$
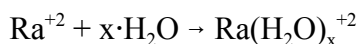
The more charged the cation, the greater is its interaction with water. Solvated cations, especially those with +4, +3, and small +2 ions, tend to act as acids by hydrolyzing in solution. Simply stated, hydrolysis is complexation where the ligand is the hydroxyl ion. To some extent, all metal cations in solution undergo hydrolysis and exist as hydrated species. The hydrolysis reaction for a metal ion is represented simply as (Choppin et al., 1995):

$$M^{+n} + m \cdot H_2O \rightarrow M(OH)_m^{+(n-m)} + m \cdot H^{+1}$$

Hydrolysis of the ferric ion (Fe^{+3}) is a classical example:

$$Fe^{+3} + H_2O \rightarrow Fe(OH)^{+2} + H^{+1}$$
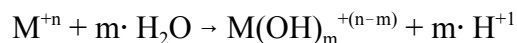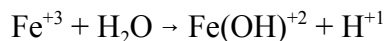
Considering the hydrated form of the cation, hydrolysis is represented by:

$$M(OH_2)_x^{+n} \rightarrow M(OH_2)_{x-1}(OH)^{(n-1)+} + H^{+1}$$
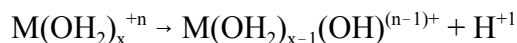
In the latter equation, the hydrated complex ion associated with the hydroxide ion, is known as the aquo-hydroxo species (Birkett et al., 1988). As each equation indicates, hydrolysis increases the acidity of the solution, and the concentration of the hydrogen ion (pH) affects the position of equilibrium. 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 Th^{+4} cation, 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). 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 (+4) 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):

$$An^{+4} > AnO_2^{+2} > An^{+3} > AnO_2^{+1}$$
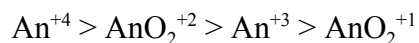
where "An" represents the general chemical symbol for an actinide.

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:

$$U^{+4} + H_2O \rightarrow U(OH)^{+3} + H^{+1}$$

$$U(OH)^{+3} + H_2O \rightarrow U(OH)_2^{+2} + H^{+1}$$
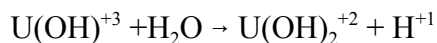
This process can, in some cases, conclude with the precipitation of an insoluble hydroxide, such as ferric hydroxide. "Soluble hydrolysis products are especially important in systems where the cation concentrations are relatively low, and hence the range of pH relatively wide over which

such species can be present and can profoundly affect the chemical behavior of the metal" (Baes and Mesmer, 1976).

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):

• 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). 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, because 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):

$$2 \, M(H_2O)_{x-1}(OH)^{+(n-1)} \rightarrow [(H_2O)_{x-2}M(OH)_2M(H_2O)_{x-2}]^{+2(n-1)} + 2 \, H_2O$$
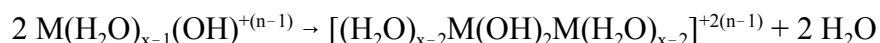
The polymers contain -OH-bridges between the metal ions that, under high temperature, prolonged aging, and/or high pH, can convert to -O-bridges, leading eventually to precipitation of hydrated metal oxides. Birkett et al. (1988) states that:

"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."

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

Many radionuclides exist as metal ions in solution and 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) (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). "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). 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).

Crouthamel and Heinrich (1971) 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"

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."

Isotope dilution analysis uses a known amount of radionuclide to determine an unknown mass of stable nuclide of the same element. 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. Due 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:

$$A + Ms \rightarrow A \cdot Ms$$
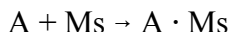
where A is the normal reacting molecule or ion, and Ms is the masking agent. The decreased concentration of A at equilibrium determines the efficiency of masking. An excess of masking agent favors the completeness of masking, as expected from LeChatelier's Principle. Feigl (1936) has described masking reagent and the masking of a reaction:

> "... 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) and in Dean (1995).

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 interferent 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 Technologies, 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 14.16 and 14.17 list common masking agents.

TABLE 14.16 — Masking agents for ions of various metals

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
Cs	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

Metal	Masking Agent
La	Citrate, EDTA, F^-, oxalate, tartrate, tiron
Mg	Citrate, $C_2O_4^{-2}$, cyclohexane-1,2-diaminetetraacetic acid, *N,N*-dihydroxyethylglycine, EDTA, F^-, glycol, hexametaphosphate, OH^-, $P_2O_7^{-4}$, triethanolamine
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^{+2} with $NH_2OH\cdot HCl$ or hydrazine, sulfosalicylate, tartrate, triethanolamine, triphosphate, tiron
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
Nb	Citrate, $C_2O_4^{-2}$, F^-, H_2O_2, OH^-, tartrate
Nd	EDTA
NH_4^+	HCHO
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
Np	F^-
Os	CN^-, SCN^-, thiourea
Pa	H_2O_2
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
Pd	Acetylacetone, citrate, CN^-, EDTA, I^-, NH_3, NO_2^-, SCN^-, $S_2O_3^{-2}$, tartrate, triethanol-amine
Pt	Citrate, CN^-, EDTA, I^-, NH_3, NO_2^-, SCN^-, $S_2O_3^{-2}$, tartrate, urea
Pu	Reduction to Pu^{+4} with sulfamic acid
Rare Earths	$C_2O_4^{-2}$, citrate, EDTA, F^-, tartrate
Re	Oxidation to perrhenate
Rh	Citrate, tartrate, thiourea
Ru	CN^-, thiourea
Sb	Citrate, 2,3-dimercaptopropanol, EDTA, I^-, OH^-, oxalate, S^{-2}, S_2^{-2}, $S_2O_3^{-2}$, tartrate, triethanolamine
Sc	Cyclohexane-1,2-diaminetetraacetic acid, F^-, tartrate
Se	Citrate, F^-, I^-, reducing agents, S^{-2}, SO_3^{-2}, tartrate
Sn	Citrate, $C_2O_3^{-2}$, 2,3-dimercaptopropanol, EDTA, F^-, I^-, OH^-, oxidation with bromine water, PO_4^{-3}, tartrate, triethanolamine, thioglycolic acid
Ta	Citrate, F^-, H_2O_2, OH^-, oxalate, tartrate
Te	Citrate, F^-, I^-, reducing agents, S^{-2}, sulfite, tartrate
Th	Acetate, acetylacetone, citrate, EDTA, F^-, SO_4^{-2}, 4-sulfobenzenearsonic acid, sulfosalicylic acid, tartrate, triethanolamine
Ti	Ascorbic acid, citrate, F^-, gluconate, H_2O_2, mannitol, $Na_5P_3O_{10}$, OH^-, SO_4^{-2}, sulfosalicylic, acid, tartrate, triethanolamine, tiron
Tl	Citrate, Cl^-, CN^-, EDTA, HCHO, hydrazine, $NH_2OH\cdot HCl$, oxalate, tartrate, triethanolamine
U	Citrate, $(NH_4)_2CO_3$, $C_2O_4^{-2}$, EDTA, F^-, H_2O_2, hydrazine + triethanolamine, PO_4^{-3}, tartrate
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

Sources: Perrin (1979) and Dean (1995)

TABLE 14.17 — 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^{+2}
Br_2	Phenol, sulfosalicylic acid
BrO_3^-	Reduction with AsO_4^{-5}, hydrazine, sulfite, or thiosulfate
Chromate(VI)	Reduction with AsO_4^{-5}, ascorbic acid, hydrazine, hydroxylamine, sulfite, or thiosulfate
Citrate	Ca^{+2}
Cl^-	Hg^{+2}, Sb^{+3}
Cl_2	Sulfite
ClO_3^-	Thiosulfate
ClO_4^-	Hydrazine, sulfite
CN^-	HCHO, Hg^{+2}, transition-metal ions
EDTA	Cu^{+2}
F^-	Al^{+3}, Be^{+2}, boric acid, Fe^{+3}, Th^{+4}, Ti^{+4}, Zr^{+4}
$Fe(CN)_3^{-3}$	AsO_4^{-5}, ascorbic acid, hydrazine, hydroxylamine, thiosulfate
Germanic Acid	Glucose, glycerol, mannitol
I^-	Hg^{+2}
I_2	Thiosulfate
IO_3^-	Hydrazine, sulfite, thiosulfate
IO_4^-	AsO_4^{-5}, hydrazine, molybdate(VI), sulfite, thiosulfate
MnO_4^-	Reduction with AsO_4^{-5}, ascorbic acid, azide, hydrazine, hydroxylamine, oxalic acid, sulfite, or thiosulfate
MoO_4^{-2}	
NO_2^-	Citrate, F^-, H_2O_2, oxalate, thiocyanate + Sn^{+2}
Oxalate	Co^{+2}, sulfamic acid, sulfanilic acid, urea
Phosphate	Molybdate(VI), permanganate, Al^{+3}
S	Fe^{+3}, tartrate
S^{-2}	CN^-, S^{2-}, sulfite
Sulfate	Permanganate + sulfuric acid, sulfur
Sulfite	Cr^{+3} + heat
SO_6^{-2}	HCHO, Hg^{+2}, permanganate + sulfuric acid
Se and its anions	Ascorbic acid, hydroxylamine, thiosulfate
TeI^-	Diaminobenzidine, sulfide, sulfite

Anion or Neutral Molecule	Masking Agent
Tungstate	Citrate, tartrate
Vanadate	Tartrate

Sources: Perrin (1979) 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., through the oxidation of EDTA in acidic solutions by permanganate or another strong oxidizing agent).

14.10.9   Review of Specific Radionuclides

The analytical separation and analysis of radionuclides involves several scientific disciplines. The decay of one radionuclide to another is referred to as "radioactive equilibrium." A series of mathematical expressions (derived from the Bateman equations, Friedlander et al., 1981) identify three separate cases of these equilibria (see Attachment 14A, "Radioactive Decay and Equilibrium").

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. Americium-243 and ^{241}Am, alpha emitters, are the longest lived with half-lives of 7,380 years and 432.7 years, respectively. Americium-241 and ^{243}Am also undergo spontaneous fission. Americium-242m has a half-life of 141 years, and the half-lives of the remaining isotopes are measured in hours, minutes, or seconds. Americium-241 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. Americium-241 is found in various plutonium 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 (Am^{+3}). 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 AmX_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. Americium-241 is also a gamma emitter.

Americium is generally thought to be adsorbed by many common minerals at pH values found in the environment. Complexation of Am^{+3} by naturally occurring ligands, however, would be expected to strongly reduce its adsorption.

<u>Solution Chemistry</u>

Americium can exist in solution in the +3, +4, (V), and (VI) 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. In contrast, dissociation of $Am(OH)_4$ or AmO_2 [both Am^{+4}] 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(VII) in alkaline solutions from the oxidation of AmO_2^{+2}.

OXIDATION-REDUCTION BEHAVIOR. Although disproportionation reactions convert the +4 and (V) oxidation states into the +3 and (VI) 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 (VI).

The +4 state is reduced to Am^{+3} by iodide. In dilute, nonreducing solutions, peroxydisulfate ($S_2O_8^{-2}$) oxidize both the +3 and (V) states to the (VI) state. Ce^{+4} and ozone (O_3) oxidize the (V) state to (VI) 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 Am^{+3} and Am^{+4} form complexes with organic chelants. These are stable in aqueous and organic solvents. Americium (+4) 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 (VI) 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^{+3} 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^{+3}. Select oxidation of other transuranic elements such as neptunium and plutonium to the +4 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 Am^{+3} 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 (+4) is also coprecipitated with these reagents as well as with zirconium phosphate [$Zr_3(PO_4)_4$]. 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. Tributylphosphate (TBP) in kerosene or TTA in xylene removes most oxidation states of neptunium and plutonium from Am^{+3} 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. Bis(2-ethylhexyl) phosphoric acid (HDEHP) in toluene is highly effective in extracting Am^{+3} and is used in sample preparation for alpha spectroscopic analysis.

Plutonium in the +4 oxidation state can interfere with Am analysis. See Section 14.10.9.8 on plutonium for a discussion of how to separate americium from plutonium.

ION EXCHANGE. Separation of americium can be achieved by cation-exchange chromatography. Any of its oxidation states exchange with 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, Am^{+3} 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 americium. Anionic complexes of Am^{+3} form at high chloride concentrations, providing a chemical form that is easily exchanged on an anion-exchange column. The column can be eluted using dilute hydrochloric acid or a dilute hydrochloric acid/ammonium thiocyanate solution. Anion-exchange separations of americium are also realized with columns prepared with concentrated nitric acid solutions. The sequential separation of the actinides is accomplished readily using anion-exchange chromatography. Americium, plutonium, neptunium, thorium, protactinium, curium, and uranium can all be separated by the proper application of select acid or salt solutions to the column.

ELECTRODEPOSITION. Americium can be electrodeposited for alpha spectrometry measurement on a highly polished platinum cathode. The sample is dissolved in a dilute hydrochloric acid solution that has been adjusted to a pH of about six with ammonium hydroxide solution using methyl red indicator. The process runs for one hour at 1.2 amps.

Methods of Analysis

Americium-241 is detected and quantified by alpha or gamma spectrometry, or by gas proportional counting (GPC). Trace quantities of [241]Am are analyzed by GPC, after separation from interfering radionuclides by solvent extraction, coprecipitation, or ion-exchange chromatography. The isolated radionuclide is collected and mounted on a planchet or

electroplated onto a platinum electrode for counting by alpha spectrometry. Americium-243 is added to the analytical solution as a tracer to measure chemical yield. Americium-241 may be determined directly (i.e., no radiochemical separation) in bulk soil samples by gamma spectroscopy.

> Compiled from: Ahrland, 1986; Baes and Mesmer, 1976; Choppin et al., 1995; Considine and Considine, 1983; Cotton and Wilkinson, 1988; DOE, 1990 and 1997, 1995; 1997; Ehmann and Vance, 1991; Greenwood and Earnshaw, 1984; Haissinsky and Adolff, 1965; Horwitz et al., 1993, 1995; Katz et al., 1986; Lindsay, 1988; Metz and Waterbury, 1962; NEA, 1982; SCA, 2001; Penneman, 1994; Penneman and Keenan, 1960; Schulz and Penneman, 1986; Seaborg and Loveland, 1990.

14.10.9.2   Carbon

The chemistry of carbon compounds is too extensive to be summarized here. Fortunately, only one isotope of carbon, ^{14}C, is significant in analytical separation. This chapter will focus on the two principal radioisotopes of carbon that are in use: ^{11}C and ^{14}C.

Isotopes

Carbon-11 has a half-life of 20 minutes. It is used for medical diagnoses and is prepared by proton bombardment of a boron target in an accelerator. The ^{11}C in the target then may be incorporated as part of a tracer molecule that would be used for the diagnosis. This isotope is also formed in nuclear reactors by the two reactions, $^{11}B(p, n)\ ^{11}C$ and $^{12}C(n, 2n)^{11}C$.

The chemical environment in the reactor coolant system is highly reducing (overpressure of hydrogen gas is used to minimize oxygen formation from radiolysis of water). Thus, the chemical form of the carbon is most likely $^{11}CH_4$. The radioisotope decays to ^{11}B by positron emission. It may be detected by liquid scintillation or gamma ray detection of the 511 keV annihilation peak. Its short half-life obviates the need for its environmental analysis.

Carbon-14 is also formed as a result of activation in reactor coolant systems of fission reactors from the following reaction: $^{17}O(n,\alpha)^{14}C$. As with ^{11}C, the chemical form will most likely be $^{14}CH_4$.

Occurrence

Carbon-14 is a naturally occurring radionuclide with a half-life of 5,720 years. It is formed as a result of $^{14}N(n, p)^{14}C$. The nitrogen atoms in the upper atmosphere are bombarded with high-energy neutrons emitted from the sun. The carbon becomes incorporated as part of a CO_2 molecule due to the presence of oxygen and many highly energetic particles and free radicals in the upper atmosphere. Carbon dioxide freely exchanges with all carbon using organisms in the

environment. The living organism rapidly reaches a state of equilibrium with the environment because of the long half-life of the carbon. The rate of radioactive decay of naturally occurring ^{14}C is approximately 780 Bq (13 dpm) per gram of total carbon. However, once an organism dies, it ceases to exchange that carbon with the environment. Thus, the activity per gram of carbon would decrease with the characteristic half-life of ^{14}C (as long as the material is undisturbed). This is the basis for carbon dating of materials.

Solubility and Solution Chemistry

Organic compounds have a vast range of chemical and physical properties. Many of the ^{14}C containing materials one encounters will be insoluble in aqueous solution, but soluble in some organic solvents. Carbon is basically tetravalent in all compounds, and forms covalent bonds. Thus, when using separation techniques involving a carrier, such as CO_3^{-2}, it is necessary to ensure not only that the sample is dissolved, but that sufficient oxidative power has been employed to convert the analyte to the same chemical form. Carbon is also unique in that CO_2 is a common oxidation product of carbon and can easily escape from solution. The equilibria

$$CO_2 + H_2O \rightarrow HCO_3^{-1} + H^+$$

$$HCO_3^{-1} + H_2O \rightarrow CO_3^{-2} + H^+$$
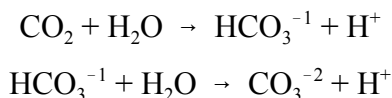
demonstrate the significant effect that acid concentration can have on the loss of carbon, as CO_2, from solution. This must be taken into consideration whenever processing ^{14}C samples.

Dissolution

Many applications involve ^{14}C as tracers. As discussed later, no sample dissolution may be needed and analysis by one of the two analytical techniques may proceed directly.

Dissolution of samples containing ^{14}C where other isotopes are present involves the complete destruction of the organic matter in the sample, and simultaneously not allowing the volatilization of the carbon. This is most commonly achieved by permanganate oxidation in a basic solution. As seen in the equilibrium equations for carbon, in basic solution it is present as the CO_3^{-2} species, which is nonvolatile.

Samples also may be prepared by high temperature oxidation, in which the carbon is converted to CO_2. The exit gasses from the combustion process must be directed through a trap which will remove carbon dioxide. These include such materials as molecular sieve, barium chloride solutions or Ascarite$^®$ columns.

Methods of Analysis

Carbon-14 decays only by β^- emission. The $E_{\beta max}$ of this emission is 0.156 MeV. Although it is detectable by gas proportional counting, the only two methods of analysis commonly used for this isotope are liquid scintillation and mass spectroscopic analysis. The methods for liquid scintillation analyses are described in Chapter 15, *Quantification of Radionuclides*, and Kessler (1989).

14.10.9.3   Cesium

Cesium is the last member of the naturally occurring alkali metals in Group IA of the Periodic Table, with an atomic number of 55. Its radiochemistry is simplified because the Group IA metals form only +1 ions. Elemental cesium is a very soft, silver-white metallic solid in the 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. With sufficient air, it ignites spontaneously. It is normally stored under xylente or toluene to prevent contact with air.

Isotopes

Cesium isotopes of mass number 112 to 148 have been identified. Cesium-133 is the only stable isotope. Cesium-134, ^{136}Cs and ^{137}Cs are the only isotopes of significance from an environmental perspective. They are formed from the nuclear fission process. Their half-lives are 2.06 years, 13.2 days, and 30.17 years, respectively. Cesium-135 also is formed as a result of the fission process. However, it is not a significant isotope, because it is a low-energy (0.21 MeV) beta-only emitter with a long half-life (2.2×10^6 years).

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-137 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's 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. Cesium-137 has replaced ^{60}Co in the treatment of cancer and has been used in industrial radiography for the control of welds. Cesium-137 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 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.

Cesium-137, 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 irreversibly 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 TTA in 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 milliliter 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 electro-static 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 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 ^{137m}Ba. However, because 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). Cesium-137 is used as part of a group of nuclides in a mixed radioactivity source for calibration of gamma ray spectrometers. It is also used in some liquid scintillation spectrophotometers to generate a Compton distribution to determine the quench.

> 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.

14.10.9.4   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

Cobalt-59 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 principal isotopes of cobalt (with their half-lives) are ^{57}Co (t$_{1/2}$ ≈ 272 d), ^{58}Co (t$_{1/2}$ ≈ 71 d), and ^{60}Co (t$_{1/2}$ ≈ 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. Cobalt-60 is produced by neutron activation of stable ^{59}Co. Cobalt-56 and ^{57}Co are prepared by bombardment of iron or nickel with protons or deuterons. Cobalt-58 (formed by activation of nickel) is now the dominant isotope formed in nuclear power plants during a fuel cycle, because most power plants have replaced their cobalt-bearing alloys, such as stellite.

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 and other solids, as a food irradiation source for sterilization, or as an injectable radio-nuclide for the measurement of flow rates in pipes. The half-life of ^{60}Co (t$_{1/2}$ ≈ 5.2 y), and its gamma emissions make it a principal contributor to potential dose effects in storage and transport of radioactive waste.

Solubility of Compounds

Most simple cobalt compounds contain Co^{+2}, but Co^{+2} and Co^{+3} display varied solubilities in water. To some extent, their solubilities depend on the oxidation state of the metal. For example, all the halides of Co^{+2} are soluble but the only stable halide of Co^{+3}, the fluoride, is insoluble. The sulfates of both oxidation states are soluble in water. The acetate of Co^{+2} is soluble, but that of Co^{+3} hydrolyses in water. The bromate, chlorate, and perchlorate of Co^{+2} are also soluble. Insoluble compounds include all the oxides of both oxidation states, Co^{+2} sulfide, cyanide, oxalate, chromate, and carbonate. The hydroxides are slightly soluble. Several thousand complex compounds of cobalt are known. Almost all are Co^{+3} 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, Co^{+2} oxide (CoO) below 200 °C and above 900 °C and Co^{+2}-Co^{+3} oxide (Co_3O_4) between the temperature extremes. It reacts with common mineral acids and slowly with hydrofluoric and phosphoric acids to form Co^{+2} 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. Co^{+2} 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. Cobalt-60 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, Co^{+2} 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 Co^{+2}:

$$4\ Co^{+3} + 2\ H_2O \rightarrow 4\ Co^{+2} + O_2 + 4\ H^{+1}$$
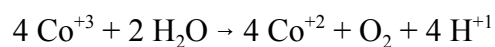
Complexation of Co^{+3} decreases its oxidizing power and most complex ions of the +3 oxidation state are stable in solution.

COMPLEXATION. Several thousand complexes of cobalt have been prepared and extensively studied, including neutral structures and those containing complex cations or anions. 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 Co^{+2}, $[Co(H_2O)_6]^{+2}$, 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 Co^{+3} 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 Co^{+3} hexamine complex forms according to:

$$4\ CoX_2 + 4\ NH_4X + 20\ NH_3 + O_2 \rightleftharpoons 4\ [Co(NH_3)_6]X_3 + 2\ H_2O$$
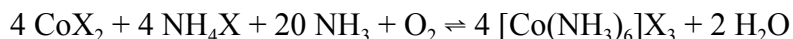
HYDROLYSIS. The hydrolysis of the +2 oxidation state of cobalt is not significant in aqueous media below pH 7. At pH 7, hydrolysis of 0.001 M solution of the cation begins and is significant at a pH above 9. The hydrolysis of the +3 oxidation state is reminiscent of the hydrolysis of Fe^{+3}, but it is not as extensive. Hydrolysis of Co^{+3} is significant at pH 5. In contrast, the hydrolysis of Fe^{+3} 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: heating $K_3[Co(NO_2)_6]$ after standing for some time makes it unstable). 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 from interfering metals. Nickel can interfere with this precipitation, but can be removed with dimethylglyoxime. Precipitation of Co^{+2} as mercury tetracyanato-cobaltate (+2) {$Hg[Co(SCN)_4]$} 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 hydro-fluoric acid (HF), hydrochloric acid, and calcium chloride ($HCl/CaCl_2$), hydrobromic acid (HBr), hydroiodic acid (HI), or ammonium thiocyanate (NH_4SCN). For example, Co^{+2} has been separated from Ni^{+2} 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 Fe^{+3} by first masking the iron with citrate.

Several chelate compounds have been used to extract cobalt from aqueous solutions. Acetyl-acetone (acac) forms a chelate with Co^{+3}, but not Co^{+2}, that is soluble in chloroform at pH 6 to 9,

permitting separation from several metals including nickel. Co^{+2} can be oxidized to Co^{+3} with hydrogen peroxide (H_2O_2) prior to extraction. The chelating agent α-nitroso-β-napthol has also been used in the separation of Co^{+3} by solvent extraction. Diphenylthiocarbazone (dithizone) has been used at pH 8 to extract cobalt into carbon tetrachloride and chloroform after metals that form dithizonates 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. Cobalt-60 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. Co^{+2}-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.

ADSORPTION 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 Co^{+2} complexes of tartaric acid and dioxane. A complex of nitroso-*R*-salts are adsorbed onto an alumina column while other metals pass through the column. Cobalt is eluted with sulfuric acid. Cobalt dithizonates adsorb 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—kaolinite, bentonite, and montmorillonite—separate Co^{+2} from Cu^{+2}. Cu^{+2} adsorbs and Co^{+2} elutes with water. Silica gel and activated silica have both been used as adsorbents in cobalt chromatography.

Organic adsorbents such as 8-hydroxyquinoline and dimethylglyoxime have been used in cobalt-adsorption chromatographic systems. Powdered 8-hydroxyquinoline separates Co^{+2} from other cations and anions, for example, and dimethylglyoxime separates cobalt from nickel. Cobalt-cyano complexes adsorb 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.

ELECTRODEPOSITION. 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 Co^{+2}, $Co(NH_3)_6^{+2}$ in solution. Reducing agents such as hydrazine sulfate are added to prevent anodic deposits of cobalt and the oxidation of the Co^{+2}-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

Cobalt-57, ^{58}Co, and ^{60}Co maybe concentrated from solution by coprecipitation and determined by gamma-ray spectrometry. Cobalt-60 is most commonly produced by the neutron activation of ^{59}Co, in a reactor or an accelerator. Cobalt-58 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. Cobalt-58 is the most significant contributor to the gamma ray induced radiation fields in these facilities. Cobalt-57 can be produced by either of the following, $^{58}Ni(n,d)^{57}Co$ [reactor] or $^{56}Fe(d,n)^{57}Co$ [accelerator], Cobalt-57 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.

14.10.9.5   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, (V), and (VII) 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 (V) state allows readily available methods for separation and purification of radionuclides of iodine in radiochemical procedures.

Isotopes

There are 42 known isotopes of iodine, including seven metastable states. The mass numbers range from 108 to 142. The only stable isotope is naturally occurring ^{127}I. The half-lives of the radionuclides range from milliseconds to days with the single exception of long-lived ^{129}I ($t_{1/2} \approx 1.57 \times 10^7$ y). Iodine radionuclides with lower mass numbers decay primarily by electron capture. The high mass numbers are, for the most part, beta emitters. The significant radionuclides are ^{123}I

($t_{1/2} \approx 13.2$ h), ^{125}I ($t_{1/2} \approx 60.1$ d, electron capture), ^{129}I (β), and ^{131}I ($t_{1/2} \approx 8$ d, β).

Occurrence and Uses

Iodine is widely distributed, but never found in the elemental form. The average concentration in the Earth's crust is about 0.3 ppm. In seawater, iodine concentration, in the form of sodium or potassium iodide, is low (about 50 ppb), but it is concentrated in certain seaweed, especially kelp. It is also found in brackish waters from oil and salt wells. The sources are saltpeter and nitrate-bearing earth in the form of calcium iodate, well brine, and seaweed. Iodine is produced from calcium iodate by extraction of the iodate from the source with water and reduction of the iodate with sodium bisulfite to iodine. Iodine is precipitated by mixing with the original iodate liquor to cause precipitation. Iodine can also be obtained from well brine, where the iodide ion is oxidized with chlorine, and then the volatile iodine is blown out with a stream of air. Sodium or potassium iodide in seaweed is calcined to an ash with sulfuric acid, which oxidizes the iodide to iodine. Iodine from any of these processes can be purified by sublimation.

Isotopes of iodine of mass ≥ 128 may all be formed as a result of fission of uranium and plutonium. Nuclear reactors and bomb tests are the most significant sources of these radioisotopes with the exception of ^{131}I. That isotope is routinely produced for use in medical imaging and diagnosis. The isotopes released from the other sources represent a short-term environmental health hazard should there be an abnormal release from a reactor or testing of bombs.

This was the case in 1979 and 1986 when the reactor incidents at Three Mile Island and Chernobyl caused releases of radioiodines. During the former event, a ban on milk distribution in the downwind corridor was enforced as a purely preventative measure. In the latter case, significant releases of iodines and other isotopes caused more drastic, long term measures for food quarantine.

Deposits on the surface of plants could provide a quick source of exposure if consumed directly 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. Iodine-129, 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.

Iodine-131 is analyzed routinely in milk, soil and water. Iodine-129 is a low energy beta and gamma emitter, which has a very long half-life ($t_{1/2} \approx 1.47 \times 10^7$ y). 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. Iodine-131 is produced for medical purposes by neutron reaction as follows: $^{130}Te(n,\gamma)^{131}Te \rightarrow$ beta decay $\rightarrow$ ^{131}I ($t_{\frac{1}{2}} \approx 8$ d).

The major use of iodine, iodine radionuclides, and iodine compounds is in medical diagnosis and treatment. Iodine-123, ^{125}I, and ^{131}I are use for diagnostic imaging of the thyroid gland and the kidneys. Iodine-131 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:

$$2\ I_2 \rightleftharpoons I_4$$
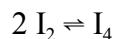
Numerous compounds of iodine are soluble in water. All metallic iodides are soluble in water except those of silver, mercury, lead, cuprous ion, thallium, and palladium. Antimony, bismuth, and tin iodides require a small amount of acid to keep them in solution. Most of the iodates and periodates are 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 electro-negative 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 oxanions, 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 (+3) hexafluoroantimonate [$(CH_3)_2I^{+3}SbF_6^{-3}$], a powerful methylating agent, is an example of the second category.

The radionuclides of iodine are radiotoxic, primarily because of their concentration in the thyroid gland. Toxicity of [129]I, if released, is a concern because of its extremely long half-life. Iodine-131, 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:

$$5\ HIO \rightleftharpoons 2\ I_2 + IO_3^{-1} + H^{+1} + 2\ H_2O$$

$$3\ IO^{-1} \rightleftharpoons 2\ I^{-1} + IO_3^{-1}$$
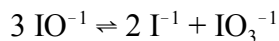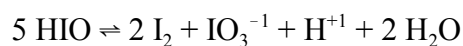
Iodine itself is not a powerful oxidizing agent, less than that of the other halogens (F_2, Cl_2, and Br_2), but its action is generally rapid. Several oxidizing and reducing agents are used to convert iodine into desired oxidation states during radiochemical procedures. These agents are used to promote 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 14.18 presents oxidizing and reducing agents commonly used in radiochemical procedures:

Table 14.18 — Common radiochemical oxidizing and reducing agents for iodine

Redox Process	Redox Reagent
$I^{-1} \rightarrow I_2$	HNO_2 ($NaNO_2$ in acid)
$I^{-1} \rightarrow IO_3^{-1}$	MnO_2 in acid
$I_2 \rightarrow I^-$	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) SO_2 gas $NaHSO_3$ and $(NH_4)_2SO_3$
$I^{-1} \rightarrow IO_4^{-1}$	$KMnO_4$ 50% CrO_3 in 18N H_2SO_4
$I^{-1} \rightarrow IO_4^{-1}$	$NaClO$ in base
$IO_4^{-1} \rightarrow I_2$	$NH_2OH·HCl$
$IO_3^{-1} \rightarrow I_2$	$NH_2OH·HCl$ $H_2C_2O_4$ in 18N H_2SO_4
$IO_4^{-1} \rightarrow I^{-1}$	$NaHSO_3$ in acid

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 state 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:

$$I_2 + I^{-1} \rightleftharpoons I_3^{-1}$$
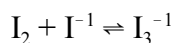
The equilibrium constant for the reaction in aqueous solution at 25 °C is 725, so appreciable concentrations of the anion can exist in solution, and the reaction is responsible for the solubility of iodine in iodide solutions.

HYDROLYSIS. Iodine hydrolyzes in water through a disproportionation reaction:

$$I_2 + H_2O \rightleftharpoons H^{+1} + I^{-1} + HIO$$
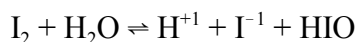
Because of the low solubility of iodine in water and the small equilibrium constant ($k=2.0\times10^{-13}$), hydrolysis produces negligible amounts of the products (6.4×10^{-6} M) even when the solution is saturated with iodine. Disproportionation of HIO produces a corresponding minute quantity of IO_3^{-1} (see the reaction above). In contrast, in alkaline solution, I_2 produces I^{-1} and IO^{-1}:

$$I_2 + 2\,OH^{-1} \rightleftharpoons I^{-1} + IO^{-1} + H_2O$$
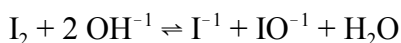
The equilibrium constant favors the products ($K = 30$), but the actual composition of the solution is complicated by the disproportionation of IO^{-1} (illustrated above), giving I^{-1} and IO_3^{-1}. The equilibrium constant for the reaction of IO^{-1} with hydroxide ion is very large (10^{20}), and 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 (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 Pd^{+4}, which will precipitate chloride. If Pd^{+2} 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 trace 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 exchanged on a cation resin and eluted with ammonium sulfite $[(NH_4)_2SO_3]$ to ensure maintenance of the iodide form. Cesium cations remain on the resin. Bulk resin also is used, and iodide is washed free of the resin also with sodium hypochlorite (NaClO) as the oxidizing agent. Anion resins provide for the exchange 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. Iodine-131 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, palladium iodide, or cuprous iodide. The last two substances are often used to determine the chemical yield in radiochemical analyses. Microquantities of ^{129}I and ^{131}I are coprecipitated with palladium iodide or cuprous iodide using stable iodide as a carrier and counted for quantification. Iodine-129 usually is beta-counted in a liquid-scintillation system, but it also can be determined by gamma-ray spectrometry. Iodine-129 can undergo neutron activation and then be measured by

gamma-ray spectrometry from the ^{130}I ($t_{1/2} \approx 12.4$ h) produced by the neutron-capture reaction. The method uses conventional iodine valence adjustments and solvent extraction to isolate the Iodine fraction. Chemically separated ^{129}I is isolated on an anion exchange resin before being loaded for irradiation. A lower limit of detection (0.03 ng) can be achieved with a neutron flux of 5×10^{14} n/cm$^2 \cdot$s for 100 seconds. Iodine-129 also can be determined directly by mass spectrometry. The measurement limit by this technique is approximately 2 femtograms. Special counting techniques, such as beta-gamma coincidence, have also been applied to the analysis of ^{129}I. Iodine-131 is determined by gamma-ray emission. Mass spectrometry has been used for measurement of ^{125}I and ^{129}I.

> Compiled from: Adams, 1995; APHA, 1998; Armstrong et al., 1961; Bailar et al., 1984; Bate and Stokely, 1982; 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; McCurdy et al., 1980; Strebin et al., 1988.

14.10.9.6 Neptunium

Neptunium, atomic number 93, is a metal and a member of the actinide series. The relatively short half-lives of the neptunium isotopes obviate naturally occurring neptunium from being detected in environmental samples (except in some rare instances). Thus, all detected isotopes are produced artificially, principally by neutron bombardment of uranium. Neptunium has six possible oxidation states: +2, +3, +4, (V), (VI), and (VII). The most stable ionic form of neptunium is the NpO$_2^{+1}$ ion. The ionic states of neptunium are similar to that of manganese, however the chemistry is most closely associated with uranium and plutonium.

Isotopes

There are 17 isotopes of neptunium, which include three metastable states. The mass range of neptunium isotopes is from 226 to 242. All isotopes are radioactive, and the longest-lived isotope, ^{237}Np, has a half-life of 2.1×10^6 years and decays by alpha emission (principal decay mode) or spontaneous fission (very low probability of occurrence). The most common mode of decay for the other neptunium isotopes is by β-particle emission or electron capture.

Neptunium is formed in nuclear reactors from two separate neutron-capture reactions with uranium. Thus the largest quantity of neptunium isotopes are associated with spent nuclear fuel. In fuel reprocessing, the focus is on the recovery of uranium and plutonium isotopes. Thus the neptunium isotopes are part of the waste stream from that process.

The short-lived ^{239}Np can be used as a tracer when separated from its parent ^{243}Am. With the half-life of the americium at 7,370 years, and that of the neptunium is only 2.3 days, tracer quantities can be successfully removed every 6–10 days from an americium source.

Occurrences and Uses

Neptunium was the first of the actinides to be produced synthetically (in 1940). Neptunium-239 ($t_{1/2} \approx 25$ min) resulted from neutron bombardment of natural uranium.

Neptunium-237 is formed as a result of successive neutron capture on a ^{235}U nucleus to form ^{237}U. This uranium isotope has a reasonably short half-life (6.75 d). After a ^{235}U target has been irradiated with neutrons, most of the ^{237}U activity will have decayed to ^{237}Np after about 30 days (no radiochemical equilibrium; see Attachment 14A, "Radioactive Decay and Equilibrium"). At that time, the ^{237}Np may be "milked" from the source.

Neptunium-237 ($t_{1/2} \approx 2.1 \times 10^6$ y), is irradiated with neutrons to form ^{238}Np, which decays to ^{238}Pu. Plutonium-238 is used in space vehicles as a power source because of its superior energy characteristics. Neptunium-237 can be used in neutron detection equipment because it has a significant (n,γ) capture cross-section. The ^{238}Np produced has a half-life of 2.1 days with easily determinable beta or gamma emissions.

Solubility of Compounds

Neptunium solubility is strongly dependent upon oxidation state. The +3 and +4 states form very insoluble fluorides, while the (V) and (VI) states are soluble. This property is an effective means of separation of neptunium from uranium. Neptunium (+4) may be carried on zirconium phosphate precipitate, indicating its insolubility as a phosphate only in that oxidation state.

Neptunium forms two oxides, NpO_2 and Np_3O_8, both of which are soluble in concentrated hydrochloric, perchloric and nitric acids. The most soluble of the neptunium compounds are $Np(SO_4)_2$, $Np(C_2O_4)_2$, $Np(NO_3)_5$, $Np(IO_3)_4$, and $(NH_4)_2Np_2O_7$. Neptunium (+3) compounds are easily oxidized to Np^{+4} when exposed to air.

Review of Properties

Neptunium is a silvery, white metal, which is rapidly oxidized in air to the NpO_2 compound. NpF_3 is formed by the action of hydrogen and HF on NpO_2. NpF_4 is formed by the action of oxygen and HF on NpF_3. These reactions, and similar ones for the other halides take place at ~500 °C. All the halides are volatile above 450 °C, with the hexafluoride boiling at 55 °C. All the halides undergo hydrolysis in water to form the oxo-complex or ions.

Neptunium is found in the environment at very low concentrations due to the short half-lives of its isotopes and the few reactions through which ^{237}Np, its long-lived isotope, can be formed. The principal nuclear reactions are identified here:

$$^{238}U(n, 2n)^{237}U \rightarrow {}^{237}Np + \beta^-$$

$$^{235}U(n,\gamma) \rightarrow {}^{236}U(n,\gamma) \rightarrow {}^{237}U \rightarrow {}^{237}Np + \beta^-$$
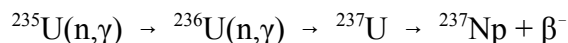
Solution Chemistry

Neptunium most closely resembles uranium in its solution chemistry, although it has many differences that allow it to be easily separated. The +4 and (V) oxidation states are the two most commonly encountered in chemical and environmental analysis of neptunium.

COMPLEXATION. Neptunium forms complexes with fluorides, oxalates, phosphates, sulfates, and acetates in the +4 oxidation state at the macro level. However, for chemical separation of neptunium in concentrations found in environmental samples, the sulfate or the fluoride of the +4 oxidation state can be co-precipitated with $BaSO_4$ or LaF_3, respectively.

Neptunium (+4) also forms strong complexes in HCl and HNO_3 with the chloride and nitrate anions. These complexes appear to have similar complexation constants and charge densities as those of U(VI) and Pu(VI) in the same media. Neptunium(V) forms weak complexes with oxalate ions. Complexation in basic media with potassium phosphotungstate or lithium hydroxide has been shown to be a useful method for oxidation-reduction potential measurements as the individual oxidation states are stabilized significantly.

OXIDATION-REDUCTION. The most stable oxidation state of neptunium in aqueous solution is (V). Oxidation in basic solution to (VI) can be achieved with MnO_4^-, or BrO_3^-. Like manganese, neptunium can form the (VII) state. This can be achieved in basic solution with nitrous oxide, persulfate, or ozone.

Solutions of Np(V) can undergo disproportionation to yield the (VI) and +4 oxidation states. This reaction has a small equilibrium constant. However, in sulfuric acid media this may be accelerated a thousand fold, because sulfates complex with the Np^{+4} ion, driving the disproportionation reaction towards completion.

Dissolution of Samples

The dissolution of samples containing neptunium must be rigorous in ensuring complete dissolution, because no stable isotopes of neptunium exist to act as carriers. High temperature furnace oxidation of soil, vegetable, and fecal samples will ensure that the neptunium will be in the (VI) oxidation state. The resultant ash can be dissolved using lithium metaborate or perchloric acid. At that point it may be selectively reduced to either the (V) or +4 oxidation state, depending upon the other analytes from which it must be separated.

Separation Methods

PRECIPITATION AND COPRECIPITATION. The only samples that will have a significant amount of

neptunium will be high-level wastes (HLW) resulting from spent fuel. Thus, for other sample analyses, the methods of precipitation of neptunium usually involve the use of a co-precipitant. In this respect, neptunium acts just like uranium. The +4 oxidation state is the one that will co-precipitate with LaF_3. If Np(V) or (VI) are formed, they will not precipitate with fluoride but stay in solution. This is analogous to the chemistry of the U^{+4} and U(VI) ions in solution.

Neptunium, like the other actinides, will flocculate with a general precipitating reagent such as iron hydroxide or titanium hydroxide.

SOLVENT EXTRACTION. Neptunium can be extracted into organic solvents such as methyl isobutyl ketone (MIBK), TBP, xylene and dibutoxytetraethylene glycol. The +4, (V), and (VI) oxidation states are extracted using these solvents under a variety of conditions. In all cases, care must be taken to eliminate or mask any fluorides, oxalates, or sulfates that are present, because they will have a significant effect on the extraction efficiency. The extraction process is aided by complex-forming compounds such as TTA, TIOA, trioctylphosphine oxide (TOPO), or tributylamine (TBA). Several different methods have been developed that use combinations of these chelates as well. In these instances a synergistic effect has been noted.

ION-EXCHANGE CHROMATOGRAPHY. The four principal neptunium oxidation states are soluble in dilute to concentrated HCl, $HClO_4$, HNO_3, and H_2SO_4. Although neptunium forms complexes with these ions in solution the exchange constant for a cation exchange resin is much greater, and the Np ions are readily removed for the aqueous system. The elution pattern of the oxidation states is, as with the other transuranics, lowest to highest ionic charge density. Thus the most strongly retained is the +4:

$$NpO_2^+ < NpO_2^{2+} < Np^{3+} < Np^{4+}.$$
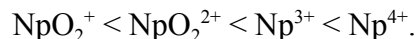
Neptunium can be separated effectively from uranium and plutonium using an anion exchange method. The plutonium and neptunium are reduced to the +4 state with uranium as (VI) in HCl. The uranium elutes, while the neptunium and plutonium are retained. The plutonium may then be reduced to the +3 state using iodide or hydrazine, and will be eluted off the resin in the HCl solution.

More recently, resin loaded with liquid extractants has been used very successfully to separate the actinides. Neptunium can be separated selectively from plutonium and uranium using a TEVA® column, after the neptunium has been reduced to the +4 state using ferrous sulfamate. This process has been shown to be successful for water, urine, soil, and fecal samples.

Methods of Analysis

Neptunium-237 is the radioisotope most commonly used as a tracer for neptunium recovery. The principal means of detection of this isotope is alpha spectrometry following a NdF_3 or LaF_3 coprecipitation step. The 4.78 MeV alpha peak is easily resolved from other alpha emitters

(notably plutonium) whose chemistry is analogous to that of neptunium. The ^{239}Np radioisotope could also be used as a tracer. It could be isolated from the parent ^{243}Am source, whose characteristic gamma-ray of 106 keV is used for quantitation. The other neptunium isotopes are most easily determined after separation and appropriate sample mounting using gas flow proportional counting.

Compiled from: Horwitz et al., 1995; Morss and Fuger, 1992; Sill and Bohrer, 2000.

14.10.9.7 Nickel

Isotopes

Twenty-four isotopes of nickel exist from mass number 51 to 74. It has five stable isotopes, and the most significant of its radioisotopes are ^{63}Ni ($t_{1/2} \approx 100$ y) and ^{59}Ni ($t_{1/2} \approx 7.6 \times 10^4$ y). All other isotopes have half-lives of 5 days or less.

Occurrence

Nickel is found in nature as one of two principal ores, pentlandite or pyrrhotite. It is also a significant constituent of meteorites. It is a silvery white metal used in the production of Invar, Hastalloy, Monel, Inconel and stainless steels. Its other principal use is in coins. Corrosion resistant alloys containing nickel are used in the fabrication of reactor components. During the life cycle of the reactor, the nickel is converted to the two long-lived radionuclides through the following reactions: ^{58}Ni(n,γ)^{59}Ni and ^{62}Ni(n,γ)^{63}Ni.

The *Code of Federal Regulations* (Title 10, Part 61) identifies these isotopes as having specific limits "in activated metal,"because the material must be physically sampled and dissolved in order to assess the level of contamination of these isotopes in the metal.

Nickel-63 is a key component in the electron-capture detector of gas chromatographic systems. This technique is used particularly for organic compounds containing chlorine and phosphorus. Nickel-63 decays by emission of a low-energy beta ($E_{\beta max} = 0.066$ MeV), which establishes a baseline current in the detector system. When a compound containing phosphorus or chlorine passes the source, these elements can "capture an electron." The response to this event is an electrical current less than the baseline current, which is converted into a response used to quantify the amount of material.

Solubility of Compounds

The soluble salts of nickel are chlorides, fluorides, sulfates, nitrates, perchlorates, and iodides. Nickel sulfide is very insoluble and will dissolve initially from solutions at low pH. However, upon exposure to air, such solutions will form the very insoluble compound Ni(OH)S. Nickel

hydroxide is also insoluble ($K_{sp} = 2 \times 10^{-16}$) and forms a very gelatinous precipitate, which can scavenge other radionuclides. Thus, avoiding the formation of this compound is very important. Solutions of neutral pH, where nickel is suspected of being a component, should be treated with ammonia to maintain the solubility of this metal ion.

Review of Properties

Nickel metal is highly resistant to air or water oxidation. It exists in the +2 oxidation state under normal conditions. It can be oxidized to the +3 oxidation state, to NiO(OH), by treatment of Ni^{+2} with aqueous bromine in potassium hydroxide. It can exist as a +4 ion in compounds such as NiO_2 (used in NiCad batteries), by oxidation with strong oxidants such as peroxydisulfate. In the +4 oxidation state nickel is a very strong oxidant and will react with water in aqueous solutions.

Nickel metal has been used in the radiochemistry laboratory as an electrode for the galvanic plating of polonium from hydrochloric acid solutions (see Section 14.10.9.17). In these instances, the polonium is being removed as interference in the alpha analysis of uranium or plutonium.

Solution Chemistry

Acid solutions of macroscopic quantities of nickel are emerald green. This is due to the formation of the hexaaquonickel complex, which is very stable.

OXIDATION. Nickel metal will readily dissolve in most mineral acids. The exception is in concentrated nitric acid, where the metal forms a passive oxide layer resistant to normal oxidation. Under normal laboratory conditions it will only form the +2 ion.

An usual property of nickel metal is that it forms a volatile carbonyl complex (boiling point 50 °C) when treated with carbon monoxide gas at low temperatures. This carbonyl compound decomposes to nickel metal at 200 °C. Thus, for samples with a high organic content that may be placed in a furnace for combustion, a high flow of air or oxygen should be assured if nickel is going to be analyzed for in the residue.

COMPLEXATION. Nickel forms strong complexes with nitrogen containing compounds such as ammonia, ethylene diamine, EDTA, and diethylenetriamine. The complex with ammonia forms a deep blue color distinct from the green color of the normal aqueous ion. The nickel ammonia complex has a large formation constant and is very stable in the pH range 7–10. This particular property of nickel is used to separate it from other metals and transuranics that may precipitate in ammonaical solution at this pH.

Nickel forms a weak complex with chloride ion as the tetrachloronicollate (+2) anion. This forms the basis of its separation from other first row transition elements iron and cobalt. The complex, $Ni^{+2} + 4Cl^- \rightarrow NiCl_4^{-2}$, is only stable in solutions greater than 10 M in HCl (see ion exchange

section). Nickel forms complexes with the chelating agent diphenylthiocarbazone, which can be extracted into organic solvents to form the basis of a separation form other transition metals.

Dissolution of Samples

Samples containing nickel radionuclides are most likely to be corrosion products, pure metals that have been irradiated, or environmental water or soil samples. Dissolution of nickel and its compounds from these matrices can be achieved using any combination of concentrated mineral acids.

Separation Methods

PRECIPITATION. The classical method of nickel determination by gravimetric analysis is through precipitation with dimethylglyoxime (DMG). This material is very specific to nickel and forms a crystalline precipitate that is easily dried and weighed. The precipitation is carried out at pH 2-3, in the absence of other macroscopic metal contaminants. Aluminum, iron, and chromium can interfere but can be sequestered at pH 7–10 in ammoniacal solution with added citrate or tartrate. The Ni-DMG precipitate may be dried, weighed, and the mass used as the determination for yield of added nickel carrier.

SOLVENT EXTRACTION. Among the many solvent extraction methods for nickel, the following compounds are notably efficient: Cupferron, acetylacetone, TTA, dibenzoylmethane, and 8-hydroxyquinoline. The extractions almost uniformly are most effective at pH 5–10. Unfortunately, in each of these separation techniques, the most effective solvents are chloroform, benzene, or carbon tetrachloride, all of which have been phased out as analytical aids in separation analysis.

ION EXCHANGE. Nickel can be separated from other transition metals on an anion exchange column by dissolution of the sample in 12 M HCl. After the sample is loaded onto the column, lowering the HCl concentration to 10 M will elute the nickel.

Nickel also can be separated from cobalt in oxalate media using a cation exchange resin. The cobalt forms an anionic complex with the oxalate while the nickel does not. The cobalt passes through the resin and the nickel is retained.

Methods of Analysis

The ^{59}Ni and ^{63}Ni isotopes do not emit gamma radiation. Liquid scintillation or proportional counting after radiochemical separation can determine both isotopes. Nickel-59, as a very thin test source, also can be determined using a low energy gamma/X-ray detector. It decays by electron capture, and yields a characteristic X-ray of 6.93 keV. In a ^{63}Ni analysis, if ^{59}Ni is present in the test source, a correction for the liquid scintillation yield of the ^{59}Ni will be

necessary. Chemical yield is determined by using a stable carrier and gravimetric analysis or spectrophotometric techniques.

Compiled from: Cotton and Wilkinson, 1966; Freiser, 1983; Kraus and Nelson, 1958; Minczewski et al., 1982.

14.10.9.8   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. Plutonium-238, ^{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. Plutonium-239 and ^{241}Pu are fissile materials—they can be split by both fast and slow neutrons. Plutonium-240, and ^{242}Pu are fissionable but have very small neutron fission cross-sections. Plutonium-240 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 result 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. Uranium-239 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^{+3} 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^{+3} and Pu^{+4}. 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: +3, +4, (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. Outside the body, however, it does not present a significant radiological hazard, because it emits only alpha, low-energy 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 made 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 (≤ 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 coastal 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 radio-chemistry. Of the five oxidation states that plutonium may have, 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 (VII) 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. Table 14.19 provides a convenient method of preparation of each state and illustrates the use of redox reagents in plutonium chemistry.

Table 14.19 — Redox agents in plutonium chemistry

Oxidation State	Form	Method of Preparation
+3	Pu^{+3}	Dissolve Pu metal in HCl and reduce Pu^{+4} with NH_2OH, N_2H_4, SO_2, or by cathodic reduction
+4	Pu^{+4}	Oxidize Pu^{+3} with hot HNO_3; treat Pu^{+3} or PuO_2^{+2} with NO_2^{-1}
+4	$PuO_2 \cdot nH_2O$ (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, (V), and (VI) 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 Pu^{+3} (27.2%), Pu^{+4} (58.4%), Pu(V) (0.7%), and Pu(VI) (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 (+4) 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 Pu^{+4} 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 Pu^{+4} 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 TBP. Strong chelate complexes form with EDTA, tartrate, citrate, TTA, acetylacetone (acac), and cupferron. Pu^{+4} 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 have 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 are 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^{+3} and Pu^{+4} are precipitated from acid solution by potassium or ammonium hydroxide as hydrated hydroxides or hydrous oxides. On redissolving in acid, Pu^{+4} tends to form the polymer, and high concentration of acid is needed to prevent its formation. Pu^{+4} peroxide is formed on the addition of hydrogen peroxide to Pu^{+3}, Pu^{+4}, 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^{+3} and Pu^{+4} 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^{+3} and Pu^{+4}. In contrast to lanthanum fluoride and bismuth phosphate, zirconium phosphate [$Zr_3 (PO_4)_4$] and an organic coprecipitate, zirconium phenylarsenate [$Zr(C_6H_5)AsO_4$], will coprecipitate Pu^{+4} 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 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 (<u>p</u>lutonium <u>u</u>ranium <u>r</u>eduction <u>ex</u>traction) is used in most fuel reprocessing plants to separate the radionuclides. It employs TBP, tri-*n*-butyl phosphate $[(C_4H_9O)_3PO]$, in a hydrocarbon solvent, as the extractant. The uranium fuel is dissolved in nitric acid as Pu^{+3}, and plutonium is oxidized to Pu^{+4} 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^{+3} with a nitric acid solution containing a reducing agent.

Solvent extraction chromatography, which uses an inert polymeric material as the support for adsorbed organic chelating agents, has provided an efficient, easy technique for rapidly separating plutonium and other transuranic elements. A process using CMPO in TBP and fixed on an inert polymeric resin matrix has been used to isolate Pu^{+4}. Aliquat-336® also has been used successfully. All plutonium in the analyte is adjusted to Pu^{+4}, 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 ($NH_4HC_2O_4$). Environmental samples contain Fe^{3+} that may interfere with this process and subsequently interfere with the analysis for plutonium. Ascorbic acid can be used to reduce Fe^{+3} to Fe^{+2}, which also reduces Pu^{+4} to Pu^{+3}. Alternatively, nitrite may be added after the ascorbic acid, which will not oxidize the iron but will convert the Pu^{+3} to Pu^{+4}. This process is an example of selective oxidation-reduction of plutonium and iron, and is used in many different separation schemes for plutonium, including separation from americium.

ION-EXCHANGE CHROMATOGRAPHY. Ion-exchange chromatography has been used extensively for the radiochemical separation of plutonium. All cationic plutonium species in noncomplexing 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. The most common uses of plutonium cation-exchange chromatography is concentrating a dilute solution or separating plutonium from non-exchangable impurities, such as organic or redox agents.

Anion-exchange chromatography is one of the primary methods for the separation of plutonium from other metals and the separation of the plutonium oxidation states. On a strong anion-exchange resin, for example, exchange of the higher oxidation states (+4, V, and VI) occurs at hydrochloric acid concentrations above 6 M, while elution occurs at 2 M acid. Plutonium (+3) does not absorb on the column, and Pu(VI) absorbs from 2 to 3 M hydrochloric acid solution. Plutonium can be separated from other actinides and most other elements by exchanging the plutonium cations—Pu^{+4} and Pu(VI)—onto a strong-anion resin from 6 M hydrochloric acid, and subsequently eluting the plutonium by reducing it to Pu^{+3}. Plutonium (+4) may be separated effectively on anion exchange resin in 7-8 M nitric acid as the $[Pu(NO_3)_6]^{-2}$ complex. Uranium will elute slowly in this media, and sufficient volume must be processed in order to avoid cross contamination of uranium with plutonium when the plutonium is subsequently eluted. Elution is achieved at a lower acid concentration, or by reduction to Pu^{+3}.

ELECTRODEPOSITION. Separation methods based on electrodeposition 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. This technique allows the plutonium isotopes to be resolved by alpha spectroscopy.

Methods of Analysis

Once isolated, purified, and in solution, ^{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 or neodymium fluoride. Mass spectrometry also can be used for longer-lived isotopes of plutonium. Radionuclides of ^{238}Pu, ^{239}Pu, and ^{240}Pu are determined by alpha spectrometry or gas flow proportional counting. Plutonium-241 measured by gas proportional counting. Plutonium-236 and ^{242}Pu are used as tracers for measuring chemical yield.

When analyzing most samples containing ^{238}Pu or ^{239}Pu, the analyst can use either ^{236}Pu or ^{242}Pu as a tracer. However, ^{242}Pu should be avoided as a tracer when analyzing samples that inherently contain ^{242}Pu, such as waste generated by commercial nuclear reactors. When analyzing samples that have higher (> 1 Bq) activity levels of ^{238}Pu or ^{239}Pu, most laboratories will use ^{236}Pu as a tracer because its higher-energy alpha-energy peaks (5.768 and 5.721 MeV) are well separated from the lower energy peaks of ^{238}Pu (highest alpha energy of 5.499 MeV) or ^{239}Pu. Thus, the isolated peaks of the ^{236}Pu tracer can be quantified easily,[1] and any minimum amount of ^{236}Pu peak tailing into the lower energy peaks of ^{238}Pu or ^{239}Pu (containing appreciably more counts) will not significantly affect their quantification. However, when analyzing samples containing very low concentrations of ^{238}Pu or ^{239}Pu (most environmental samples), ^{242}Pu can be used as a

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[1] It should be noted that any contribution from a tracer into the peak(s) of an analyte of interest must be quantified properly, and the affected analyte peak result corrected, to avoid a biased result or Type I error (false positive).

tracer because its highest peak energy of 4.90 MeV is about 0.2 MeV lower than the lowest peak energy of ^{238}Pu or ^{239}Pu. For such low activity samples, the ^{242}Pu activity added to the sample aliquant being processed should be more than the expected ^{238}Pu or ^{239}Pu test source activity. Therefore, any tailing of the ^{239}Pu alpha peaks into the ^{242}Pu peaks would be minimized.

> Compiled from: Baes and Mesmer, 1976; Choppin et al., 1995; Coleman, 1965; Cotton and Wilkinson, 1988; DOE 1990 and 1997; EPA 1973 and 1980; Maxwell and Fauth, 2000; Metz and Waterbury, 1962; Seaborg and Loveland, 1990; Weigel et al., 1986.

14.10.9.9 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, magnesium, calcium, strontium, and barium. Radium is the most alkaline 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 or by mass spectrometry.

Isotopes

There are 25 isotopes of radium, from ^{205}Ra to ^{234}Ra. 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. Radium-226 ($t_{1/2} \approx 1{,}602$ y) is the most abundant isotopic form. A member of the ^{238}U series, it is produced by alpha emission from ^{230}Th. Radium-226 emits an alpha particle and, in turn, produces ^{222}Rn, an inert gas that is also an alpha emitter. Radium-226 generates radon at the rate of 0.1 μL per day per gram of radium, and its radioactivity decreases at the rate of about 1 percent every 25 years. Radium-228 ($t_{1/2} \approx 5.77$ y) is produced in the ^{232}Th decay series by emission of an alpha particle from ^{232}Th itself.

Occurrence

In nature, radium is primarily associated with uranium and thorium, particularly in the uranium ores—carnotite and pitchblende, where ^{226}Ra is in radioactive equilibrium with ^{238}U and its other progeny. The widespread dispersal of uranium in rocks and minerals results in a considerable distribution of radium isotopes throughout nature. Generally found in trace amounts in most materials, the radium/uranium ratio is about 1 mg radium per 3 kg uranium (1 part radium in 3×10^6 parts uranium). This leads to a terrestrial abundance of approximately 10^{-6} ppm: 10^{-12} g/g in rocks and minerals. Building materials, such as bricks and concrete blocks for example, that contain mineral products also contain radium. With leaching from soil, the concentration is about 10^{-13} g/L in river and streams, and uptake in biological systems produces concentrations of 10^{-14} g/g in plants and 10^{-15} g/g in animals.

Uranium ores have been processed with hot mineral acids or boiling alkali carbonate to remove

radium and uranium. Extracted radium was usually coprecipitated with barium sulfate, converted to carbonate or sulfide, and solubilized with hydrochloric acid. Separation from barium was usually accomplished by fractional crystallization of the chlorides, bromides, or hydroxides, because barium salts are usually slightly more soluble. The free metal has been prepared by electrolysis of radium chloride solutions, using a mercury cathode. The resulting amalgam is thermally decomposed in a hydrogen atmosphere to produce the pure metal. The waste streams from these industrial operations contain radium, primarily as a coprecipitate of barium sulfate. Because many other natural ores also contain uranium and radium, processing can result in uranium and its equilibrium progeny appearing in a product or byproduct. Apatite, a phosphate ore, is used to produce phosphoric acid, and the gypsum byproduct contains all the radium originally present in the ore.

Radium-226 extracted from ores has historically been used in diverse ways as a source of radioactivity. It has been mixed with a scintillator to produce luminous paint, and at one time, the most common use for its salts was radiation therapy. As a source of gamma radiation, radium activity was enhanced by sealing a radium salt in a capsule that prevented escape of the gaseous progeny, ^{222}Rn, and allowing the radon to decay into its successive progeny. Two progeny are ^{214}Pb and ^{214}Bi, the principal emitters of gamma radiation in the source. For the most part, radium has been replaced in medical technology by other sources of radioactivity, but numerous capsules 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 anthropological 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 Methods," below), and crown ethers have been developed recently that selectively remove radium from an aqueous environment.

Review of Properties

Radium is 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.

Solution Chemistry

Existing exclusively in the +2 oxidation state, the chemistry of radium is uncomplicated by oxidation-reduction reactions that could produce alternate states in solution. It is made even less complicated by its weak tendency to form complex ions or hydrolyze in solution. These properties are a reflection of the small charge-to-crystal-radius ratio of 1.32, described above. In general, radiochemical equilibrium is established with carriers by stirring, followed by either standing or digesting in the cold for several minutes. Adsorption of trace amounts of radium on surfaces, however, is an important consideration in its radiochemistry.

COMPLEXATION. Radium, like other alkaline-earth cations, forms few complexes in acid solution. Under alkaline conditions, however, several one-to-one chelates are formed with organic ligands: EDTA, diethylene triamine pentaacetic acid (DTPA), ethyleneglycol bis(2-aminoethylether)-tetraacetate (EGTA), nitrilotriacetate (NTA or NTTA), and citrate. The most stable complex ion forms with DTPA. The tendency to form complexes decreases as their crystalline size increases and their charge-crystal-radius ratio decreases. Because crystalline sizes of the cations are in the order: $Ra^{+2} > Ba^{+2} > Sr^{+2} > Ca^{+2}$, radium has the least tendency to form complex ions, and few significant complexes of radium with inorganic anions are known. One notable exception is observed in concentrated sulfuric acid, which dissolves highly insoluble radium sulfate ($RaSO_4$) by forming $Ra(SO_4)_2^{-2}$.

Complex-ion chemistry is not used in most radium radiochemical procedures. Complexing agents are primarily employed as elution agents in cation exchange, in separations from barium ions by fractional precipitation, and in titration procedures. Alkaline citrate solutions have been used to prevent precipitation of radium in the presence of lead and barium carriers until complete isotopic exchange has been accomplished.

HYDROLYSIS. Similar to their behavior complex-ion formation, alkaline earths show less and less tendency to hydrolyze with increasing size of the ions, and the tendency decreases with increasing ionic strength of the solution. Therefore, hydrolysis of radium is an insignificant factor in their solution chemistry.

ADSORPTION. The adsorption of trace amounts of radium on surfaces is an important considera-tion in its radiochemistry. Although not as significant with radium as with some ions with higher charges, serious losses from solution can occur under certain conditions. Adsorption on glass is a particular problem, and adsorption on polyethylene has been reported. Adsorption gradually increases with increasing pH and depends strongly on the nature of the surface. In the extreme, 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, because 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, because 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. Because 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_3^{-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 [$Ba(IO_3)_2$], and various insoluble phosphates, fluorides, and oxalates (e.g., thorium phosphate [$Th_3(PO_4)_4$], lanthanum fluoride (LaF_3), and thorium oxalate [$Th(C_2O_4)_2$]. Lead sulfate ($PbSO_4$) can be used if a carrier-free radium preparation is required, because 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 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, because 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 because 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, because 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. Because radium does not form a chlorocomplex, it does not absorb 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 nonaqueous phase, leaving radium in the water. Radium is separated from actinium, thorium, polonium, lead, bismuth, and thallium, for example, by extracting these elements as 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 tetraphenyl-borate 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 gamma-counting.

Radium-228 can also be determined directly by gamma spectroscopy, using the gamma-rays of its progeny, ^{228}Ac, without concern for interference. Alower 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.

Radium-224 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-, beta-, or gamma-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.

14.10.9.10 Strontium

Strontium, atomic number 38, is the fourth member of the alkaline-earth metals, which includes beryllium, magnesium, calcium, strontium, barium, and radium. Like radium, it exists 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 eleventh 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. Strontium-90 is a fission product of ^{235}U, along with ^{89}Sr, and short-lived isotopes, ^{91}Sr to ^{102}Sr. Strontium-85 can be produced by irradiation of ^{85}Rb with accelerated protons or deuterons.

The beta emission of ^{90}Sr and its progeny, ^{90}Y ($t_{1/2} \approx 64$ 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. Because ^{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. Ratios of ^{88}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 air. It is stored under mineral oil to prevent oxidation.

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 divalent strontium ions. 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 increases 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 to leach strontium. 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. TTA has been used to extract carrier-free strontium at a pH greater than 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 diethyl ether with di-2-ethylhexyl phosphoric acid 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 from 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. Strontium-90 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.

Strontium does not form many anionic complextes, Thus, not many procedures use anion-exchange chromatography for separation of strontium. Strontium-90 has been separated from ^{90}Y on an anion-exchange resin pretreated with hydroxide. Strontium is eluted from 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.

Strontium-89 and ^{90}Sr are determined by analysis of their beta emissions. With a short half-life of 50.5 d, ^{89}Sr is only found in fresh fission products. Strontium-90 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. Strontium-90 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. Strontium-89 has a half-life of 50.5 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. Strontium-85 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.

Cerenkov radiation counting techniques also may be used for $^{89/90}$Sr analysis. When beta particle energies exceed the speed of light in the medium in which the beta particles are emitted, the excess energy is emitted in the energy range of 350-600 nm. In water, the energy to be exceeded is 0.263 MeV. As a practical matter, however, Cerenkov radiation counting is not very useful for beta energies less than 1 MeV beta maximum ($E_{\beta max}$) typically found in environmental laboratories. NCRP (1985) cites a 3 percent detection efficiency for a ^{204}Tl $E_{\beta max}$ of 0.764 MeV, with corresponding average beta energy of 0.240 MeV. Only at a ^{143}Pr of 0.932 MeV does the detection efficiency go to 6.2 percent—a detection efficiency of marginal usefulness as a figure of merit.

The three isotopes that are involved with this analysis are ^{89}Sr ($E_{\beta max}$ = 1.5 MeV), ^{90}Sr ($E_{\beta max}$ = 0.5 MeV), and ^{90}Y ($E_{\beta max}$ = 2.3 MeV). The analysis requires chemical separation of the strontium from the sample matrix by conventional techniques. Cerenkov counting relies on the beta energies (the ^{90}Sr beta does not contribute significantly). For example, strontium may be separated chemically as an oxalate precipitate (after yttrium has been removed by precipitation), dissolved in nitric acid, and counted immediately (yielding the counts for ^{89}Sr). After about 10 days, the sample would be recounted, yielding a total for ^{89}Sr + ^{90}Y. The value for the ^{90}Y is then determined by applying spectral interference factors for spectral overlap and appropriate background subtraction techniques. Alternatively, ^{90}Y can be separated from the strontium solution after a period of ingrowth and Cerenkov-counted to determine the ^{90}Sr concentration.

> Compiled from: Baes and Mesmer, 1976; Banavali et al., 1995; 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; NCRP, 1985; Riley, 1995; Rucker, 1991; Sunderman and Townley, 1960; Turekian and Bolter, 1966.

14.10.9.11 Sulfur and Phosphorus

The radiochemistry of sulfur and phosphorus is somewhat different than most other radioisotopes. These two elements are nonmetallic and, like carbon, can be found in many different types of compounds. These two elements are used most extensively as tracers by incorporation into organic molecules, generally as covalent-bonded atoms. Thus, they do not react as sulfur or phosphorus, but as the molecule of which they are a part. They may be present as inorganic species, which have their own peculiar chemistry.

Isotopes

Sulfur has 17 isotopes, four of which are stable. Only two of the 13 radioisotopes have significant radiochemical analytical applications. These are ^{35}S ($t_{1/2} \approx$ 87.2 d) and ^{37}S ($t_{1/2} \approx$ 5 min). Sulfur-35 decays only by beta emission with no gamma emission. Sulfur-37 decays by beta emission with a 3.1 MeV delayed gamma emission.

Phosphorus also has 17 isotopes, only one of which is stable. Its two principal radioisotopes, ^{32}P ($t_{1/2} \approx$ 14.3 d) and ^{33}P ($t_{1/2} \approx$ 25.3 d), both decay only by beta emission, with no gamma emission.

Occurrence

None of the radioisotopes of sulfur occurs naturally. They are produced by neutron activation of stable parent isotopes or by accelerator bombardment techniques. Both ^{32}P and ^{33}P are formed naturally in the upper atmosphere. The steady-state concentration of these radionuclides in rainwater is about 0.05 Bq/L. They are also produced artificially by accelerator bombardment.

Solubility and Solution Chemistry

The most stable forms of the two elements in aqueous solutions are sulfate and phosphate. However, the relatively long half-lives of the radioisotopes of S and P allow them to be incorporated easily into organic or biomolecules. In these instances, the chemical identity of the radioisotope is sacrificed for the chemical property of the molecule. For example, ^{35}S may be incorporated into these species, but each will have a distinct chemical property:

$$SO_4^{-2}, S^{-2}, CH_3\text{-}S\text{-}CH_2\text{-}CH_2\text{-}C(H)(NH_2)(COOH) \text{ [methionine]}$$

$$H\text{-}S\text{-}CH_2\text{-}C(H)(NH_2)(COOH) \text{ [cystine]}$$
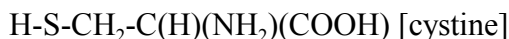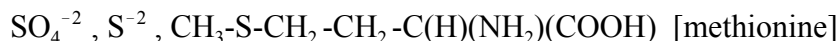
If a solution of methionine had added to it methionine labeled with ^{35}S, the radioisotope-containing molecules would be indistinguishable chemically from the other methionine molecules. However, if the methionine solution was equilibrated with a solution of $^{35}S^{-2}$, no ^{35}S would be found in the methionine molecules, because methionine does not dissociate to give S^{-2}.

Similarly, for phosphorus the radioisotope could be incorporated into the following species:

$$PO_4^{3-}, (C_8H_{17})_3PO \text{ [tri-}n\text{-octylphosphine oxide]}$$

$$H_2PO_4\text{-}\{C_9H_{14}N_5O_3\} \text{ [adenosine-5-phosphoric acid]}.$$
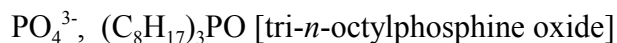
Here, the tri-*n*-octylphosphine oxide is soluble in organic solvents but not in water, while the other two are readily water-soluble. For the two water-soluble molecules, under conditions of neutral pH, no exchange of radiophosphorus would be expected between them. However under certain conditions where the organic molecule could be hydrolyzed, exchange could occur. Incorporation of the radioisotope into an organic molecule would occur by first forming the radioisotope by nuclear bombardment, then reacting the activated material with the appropriate reagents to form the molecule of interest. Attempting to form the radioisotope by activation of the organic molecule would lead to the destruction of the organic molecule, and the radioisotope would be part of other (potentially) unknown species. The chemical purity of the final product would be verified through an independent means such as infrared, nuclear magnetic resonance, or mass spectrometry. The specific activity of the new molecule then can be calculated by measuring the activity due to the radioisotope.

OXIDATION-REDUCTION. For each of these elements, the most stable ionic form in aqueous solution is as the SO_4^{-2} or the PO_4^{3-} ions (dependent upon pH). Sample oxidation for sulfur should be performed with care to avoid loss as SO_2 or as H_2S. This can occur in nitric acid when sulfides or organic sulfur compounds are present. Oxidation in basic solution using hydrogen peroxide or permanganate can avoid such losses. Phosphorus does not suffer from this disadvantage of acid oxidation. Generally, when present as phosphate or sulfate, reduction to other species will not occur unless powerful reducing agents have been added to the solution.

COMPLEXATION. Neither sulfate nor phosphate are strong complexing agents. This is due to their negative charge being spread out among many atoms, yielding low charge density. Most complexing ions are strongly nucleophilic.

Dissolution of Samples

The radioisotopes of phosphorus and sulfur generally are incorporated into *in vivo* or *in vitro* studies of plant or animal tissues. The cost common methods of sample preparation for these studies usually are maceration/suspension, tissue solubilization, and total oxidation. The method of maceration is a reduction of the "size" of the sample. The material is suspended in a minimal amount of fluid, and then a physical means such as a blender, mortar and pestle, or stirring rod is used to suspend the material in the solvent. The chemical nature of the molecule containing the radioisotope is unchanged.

Tissue solubilization is the addition of a chemical solvent such as toluene, which dissolves the tissue in its entirety putting the sample into an organic solvent matrix. The chemical nature of the molecule containing the radioisotope is unchanged.

Total oxidation is performed most frequently using either peroxide or nitric acid, which removes all of the organic material as carbon dioxide, and the elements are in solution as phosphate or sulfate. Care should be taken in this form of sample preparation for sulfur, because it can be volatilized as SO_2 or SO_3 vapor.

The molecules of interest having biochemical activity may change chemically during the course of such studies. Thus, one should consider what the potential decomposition products are, and how they should be separated from the organic/biomolecules of interest, before preparing the sample. If an environmental sample were to be analyzed for these radioisotopes, the sample preparation would need to be total-sample-oxidation, because the type of organic material would likely be unknown.

Separation Methods

Because many different organic forms exist for these elements, it would be difficult to identify all of the different separation techniques used to separate them from specific mixtures of other organic compounds. Generally, the techniques that are used are HPLC, GC, and electrophoresis. In many instances, separation of the molecules containing the radioisotopes is not necessary, because the sulfur or phosphorus is the only radioisotope present, having been used as a tracer in following the reaction progress or products.

PRECIPITATION. Sulfur may be analyzed by sample oxidation followed by barium precipitation. This takes place at about pH 2 in HCl solution. As with other separation techniques, sample processing should ensure the elimination of other cations (such as radium or strontium), which

could be present in environmental samples.

Phosphate is a strong Bronsted-Lowry base. Precipitation of phosphate salts would be carried out best in basic media. However, most metal salts also form insoluble hydroxides, so this form of separation is not used frequently. However, if other metal ions are removed, phosphate can be completely precipitated using calcium ion in basic solution.

ION EXCHANGE. Both phosphate and sulfate may be exchanged easily on anion exchange media. However, if the anion resin were in the hydroxide form, the exchange would release hydroxide and potentially cause precipitation of metal ions either on the ion exchange resin or in the eluent. Thus, converting the anion resin to the nitrate or chloride form prior to separation would permit the free flow of eluent without precipitation. Such separation will occur on weak base anion exchangers (such as those used in ion chromatography) or strong base ion exchangers.

Methods of Analysis

All of the radioisotopes of interest of phosphorus and sulfur are beta emitters. The most effective method of analysis for these isotopes is liquid scintillation. For the analysis of organic/ biomolecules, the scintillation cocktail usually may be added directly to the analyte after one of the methods of nonoxidative sample preparation described above. In some instances, these analytes may contain double-labeled compounds. Other radioisotopes, such as ^{14}C or ^{3}H, also may be incorporated into the molecule. These can also be analyzed directly by liquid scintillation because of the significant differences in the beta particle energies. Samples of unknown origin would require oxidation and separation prior to analysis.

14.10.9.12 Technetium

Technetium, atomic number 43, 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 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 γ), and ^{99}Tc (2.13×10^5 y/β to stable ^{99}Ru). Other long-lived isotopes are ^{97}Tc (2.6×10^6/electron-capture) and ^{98}Tc (4.2×10^6 y/β 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 pertechnetate (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 pertechnetate with hydrogen at 600 °C.

Potassium pertechnetates ($KTcO_4$) 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 superconductors. The corrosion protection is limited to closed systems to prevent release of the radioactive isotope. Technetium-95m, with a half-life of only 61 days, has been used in tracer work. Technetium-99m is used in medical diagnosis as a radioactive tracer. As a complex, the amount of ^{99m}Tc required for gamma scanning is very small, so it is referred to as noninvasive 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. Technetium-99m also has been used to determine the deadtime of counting detectors.

Solubility of Compounds

The nature of the compounds has not been thoroughly delineated, but ammonium pertechnetate 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.

The behavior of technetium in groundwater is highly dependent on its oxidation state. Under oxidizing conditions, pertechnetate 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 principal 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 pertechnetate 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 pertechnetate 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^{+4}], 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 because 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 pertechnetate 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 (V) 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 (V) 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 pertechnetate 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. Pertechnetate 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 tetraphenylar-senium 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. Because many other transition metals often associated with technetium also from insoluble compounds with sulfide, the method is primarily used to concentrate technetium.

Technetium (+4) 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 coprecipitated as the hexa-chlorotechnetate (+4) ($TcCl_6^{-2}$) with thallium, and rhenium as the α,α'-dipyridylhexachloro-rhenate (+4).

Technetium(VI) (probably as TcO_4^{-2}) is carried quantitatively by molybdenum 8-hydroxyquino-late and by silver or lead molybdate. Tc^{+3} 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 tetraphenyl-arsonium 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 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 from 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 most readily 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) are soluble in alcohols, ethers, ketones, and trioctylphosphine oxide or trioctylamine hydrochloride in cyclohexane or 1,2-dichloroethane. Technetium (+4), as $TcCl_6^{-2}$, extracts into chloroform in the presence of high concentrations of tetraphenylarsonium ion. Pertechnetate and perrhenate are both extracted from alkaline solution by hexone (methyl isobutyl ketone), but reduction of technetium to the +4 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 pertechnetate 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 pertechnetate and molybdate has been achieved on an anion-exchange resin in

the phosphate form where the molybdate is preferentially absorbed. Good separation of pertechnetate 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; pertechnetate is reduced to nonvolatile Tc^{+4} and remains in the acid solution. Technetium heptoxide can be separated from molybdenum trioxide by fractional sublimation at temperatures $\geq$ 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

Technetium-99 is analyzed by ICP-MS, gas proportional counting, or liquid scintillation 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. Technetium-99m ($t_{1/2}$=6.0 h), measured by gamma-ray spectrometry, can be used as a tracer for measuring the chemical yield of ^{99}Tc procedures. Conversion electron ejection 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. Molybdenum-98 is neutron-irradiated and chemically oxidized to [99]MoO_4^{-2}. This solution is ion-exchanged 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 called the "cow."

Neutron activation analysis methods for technetium have been employed since 1972. A method was developed and applied for the analysis of ^{99}Tc in mixed fission products. The method employs chemical separation of ^{99}Tc from most fission products by a cyclohexanone extraction from a basic carbonate solution. Technetium-99 is stripped into water by addition of CCl_4 to the cyclohexanone phase and then isolated on an anion exchange column. Neutron irradiation of the isolated ^{99}Tc was made in the pneumatic facility at a high flux beam reactor (e.g., at a flux of 5×10^{14} n·cm^2/sec for approximately 11 seconds. Thus, after irradiation ^{99}Tc is converted to ^{100}Tc, which, because of its 15.8 second half-life, requires an automatic process to measure its 540 and 591 keV gamma lines.

> Compiled from: Anders, 1960; Bate, 1979; CRC, 1998-99; Choppin et al., 1995; Cobble, 1964; Considine and Considine, 1983; Coomber, 1975; Cotton and Wilkinson, 1988; DOE, 1990 and 1997, 1997; Ehmann and Vance, 1991; Foti et al., 1972a, 1972b; Fried, 1995; Greenwood and Earnshaw, 1984; Hassinsky and Adloff, 1965; Kleinberg et al., 1960; Lindsay, 1988; SCA, 2001; Wahl and Bonner, 1951.

14.10.9.13 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. Thorium-232, 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 (progeny of ^{232}Th and $^{235/238}$U). The remaining isotopes are anthropogenic. 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. Thorium-232 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 (+2) [$ThFe(CN)_6$], 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 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. 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^{2}7s^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$_2$O)$_{8\text{ or }9}{}^{+4}$.

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:

$$Th^{+4} + HF \rightarrow ThF^{+3} + H^{+1}$$
$$ThF^{+3} + HF \rightarrow ThF_2{}^{+2} + H^{+1}$$
$$ThF_2{}^{+2} + HF \rightarrow ThF_3{}^{+1} + H^{+1}$$
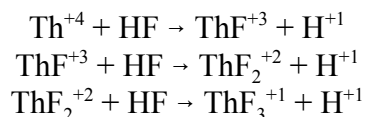
These complex ions represent the predominant species in solutions containing HF. Stable complex ions also form with oxygen-containing ligands such as nitrate, chlorate, sulfate, bisulfate, iodate, carbonate, phosphate, most carboxylate anions, and chelate anions. Some chelating agents such as salicylate, acetylacetonate (acac), 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 Th^{+4} in a saturated solution at pH 3 (approximately 5×10^{-6} M). 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 Th^{+4} cation, 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 [$Zr(IO_3)_4$], zirconium phosphate [$Zr_3(PO_4)_4$], 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 exchanged onto 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 or stainless-steel 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. TBP is usually diluted with an inert solvent such as ether or xylene/toluene 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 xylene/toluene. 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 Aliquat-336® (tricaprylylmethylammonium chloride or methyltricaprylyl-ammonium chloride), CMPO in TBP, or DPPP (dipentylpentylphosphonate), also called DAAP (diamylamylphosphonate), or 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 chromatography 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. Thorium-227, ^{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. Thorium-234 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. Thorium-229 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.

14.10.9.14 Tritium

Unlike the elements reviewed in this section, tritium is 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 hydrogen is found, with and without the other isotopes of the element (hydrogen and deuterium)—as molecular hydrogen (HT, DT, T_2), water (HOT, 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 HOT. Natural processes account for approximately one T atom per 10^{18} hydrogen atoms. The source of some natural tritium is ejection from the sun, but the primary source is from bombardment of ^{14}N with cosmic neutrons in the upper atmosphere:

$$^{14}_{7}N + ^{1}_{0}n \rightarrow ^{3}H + ^{12}_{6}C$$
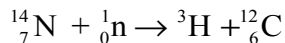
Most tritium from this source appears as HOT.

Tritium is produced in laboratory and industrial processes by nuclear reactions such as:

$$^{2}_{1}D + ^{2}_{1}D \rightarrow ^{3}_{1}T + ^{1}_{1}H$$
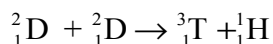
For large-scale production of tritium, ^6Li alloyed with magnesium or aluminum is the target of neutrons:

$$^{6}_{3}Li + ^{1}_{0}n \rightarrow ^{3}_{1}T + ^{4}_{2}He$$
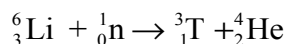
The radionuclide is retained in the alloy until released by acid dissolution of the target. Large quantities are handled as HT or HOT. HOT is formed from HT when it is exposed to oxygen or water vapor. A convenient way to store tritium is as the hydride of uranium (UT_3). It is formed by reacting the 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 boron, lithium, and deuterium:

$$^{10}B(n, T) \, 2 \, ^4He$$
$$^{11}B(n, T) \, ^9Be$$
$$^{6}Li \, (n, T) \, ^4He$$
$$^{2}H \, (n,\gamma) \, T$$
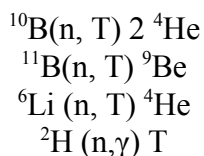
and from the fission process as a ternary fission fragment. Significant uses for tritium are in fission bombs to boost their yield, in thermonuclear weapons (the hydrogen bomb), in luminescent signs, and in night-vision military applications. Tritium bombarded with high-energy deuterons undergoes fusion to form helium and releases neutrons:

$$^{3}_{1}H + ^{2}_{1}H \rightarrow ^{4}_{2}He + ^{1}_{0}n$$
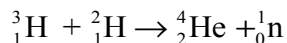
A tremendous amount of energy is released during the nuclear reaction, much more than the energy of the bombarding particle. Fusion research on controlled thermonuclear reactions should lead to an energy source for electrical generation.

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 because it does not emit gamma radiation. Hydrological studies with HOT are 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 ($t_{1/2} \approx 12.3$ y) decays 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 1.5 times 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 HOT, 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, HOT and DTO are found.

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 HOT. 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 HOT 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 HOT, 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 oxide (Cu^{+2}) 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.

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 HOT 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. In addition, tritiated water can be absorbed through the skin or wounds unless protective equipment is used. 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 HOT. 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.

Tritium found in environmental samples may be either exchangeable in acid media (labile) or organically bound. In the latter case, combustion of the material is necessary to release the tritium into an exchangeable form. This is performed usually by adding an oxidizing agent, like $KMnO_4$, if the contribution of the organic tritium to the total tritium is large.

Separation Methods

DISTILLATION. Tritium in water samples is essentially in the form of HOT. It can be removed quantitatively from aqueous mixtures by distillation to dryness, which also separate it from 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 permanganate, 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 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 (Cu_2O) 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 HOT can be reduced to TH by heating with metals, such as magnesium, zinc, or calcium, and analyzed as a gas. Conversely, if tritium is present as HT or T_2, it may be oxidized to HOT by passing the gaseous sample over a platinum, palladium, or nickel catalyst in the presence of air.

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 HOT 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 HOT 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:

$$C_4H_9MgBr + THO \rightarrow C_4H_9T + Mg(OH)Br$$
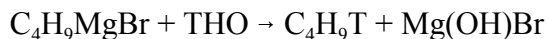
Inorganic compounds can also be use to produce gaseous products:

$$Al_4C_3 + 3\ HOT + 9\ H_2O \rightarrow 3\ CH_3T + 4\ Al(OH)_3$$
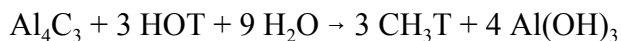
EXCHANGE. Methods to assess tritium in compounds take advantage of exchange reactions to collect the radionuclide in a volatile substance that can be collected in a gas tube for measure-ment. Acetone is one compound that easily exchanges tritium in an acid or base medium and is relatively volatile.

Methods of Analysis

Tritium is collected primarily as HOT 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. Another distillation technique involves the use of cyclohexane to form an azeotropic (low boiling point) mixture. This technique is sometimes used in analysis of biota samples. Tritium may be analyzed, indirectly, by mass spectrometry of its progeny, ^{3}He.

> Compiled from: Choppin et al., 1995; Cotton and Wilkinson, 1988; DOE, 1994; Demange et al., 2002; Duckworth, 1995; Greenwood and Earnshaw, 1984; Hampel, 1968; Hassinky and Adloff, 1965; Kaplan, 1995; Lindsay, 1988; Mitchell, 1961; Passo and Cook, 1994; Surano et al., 1992.

14.10.9.15 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. Uranium-235 (0.72%) and ^{238}U (99.27%) occur naturally as primordial uranium. Uranium-234 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, because it has the shortest half-life for each of these isotopes.

Another isotope of uranium of significance is ^{232}U (t$_{1/2}$ ≈ 69.8 y). 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.

Uranium-235 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. Uranium-238 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 known 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, from 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 (+3 and +4) are soluble, as are the chloride and bromide of U(V) [UOX_2] and the fluoride, chloride, and bromide of U(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 forms 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 +4 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, (V) and (VI); 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 (VI) 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 (V) 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 ($k = 1.7 \times 10^6$):

$$2\ UO_2^{+1} + 4\ H^{+1} \rightleftharpoons UO_2^{+2} + U^{+4} + 2\ H_2O$$

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.

Uranium(VI) 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(VI) 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:

$$U^{+4} > UO_2^{+2} > U^{+3} > UO_2^{+1},$$
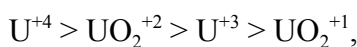
while the order of stability of the anionic complexes is represented by:

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 expected for a +3 ion of its size—a much weaker acid than most other metals ions of this charge. The U^{+4} ion is readily hydrolyzed in solution, but exists as the unhydrolyzed, hydrated ion in strongly acidic solutions. Hydrolysis begins at pH<1, starting with the $U(OH)^{+3}$ species. As pH increases, 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 carried 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. Such mixtures have been known to detonate if the perchloric acid is allowed to dry out.

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 from 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 include:

- Ammonium hydroxide, which precipitates uranium quantitatively at pH $\geq$ 4;
- Carbonate [however, it will form soluble anionic complexes with U(VI) at pH 5 to 11 while many other metals form insoluble hydroxides];
- Peroxide;
- Oxalic acid, which completely precipitates uranium (+4) while U(VI) forms a soluble complex;
- Iodide;
- Iodate;
- Phosphate for U(VI) over a wide pH range;

- Sulfate;
- Cupferron, which precipitates uranium (+4) from an acidic solution but U(VI) from a neutral solution; and
- 8-hydroxyquinoline, which forms a quantitatively precipitate with U(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 U(VI) coprecipatate with ceric and thorium fluoride, calcium, zirconium, and aluminum phosphate, barium carbonate, thorium hexametaphosphate, magnesium oxide, and thorium peroxide. Uranium (+4) 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. They 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, 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 xylene/toluene, 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^{+3} 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 U(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 upon the salt used, its 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 U^{+4} for subsequent extraction. Other chelating agents used to extract uranium include 8-hydroxyquinoline, acetylacetone in hexone, or chloroform.

Amines with molecular weights in the 250 to 500 range are used to extract anionic complexes of U(VI) from acidic solutions. The amine forms a salt in the acidic medium consisting of an ammonium cation and complex anion, $(C_{10}H_{21})_3NH^{+1} UO_2(NO_3)^{-1}$, for example. Selectivity of the amines for U(VI) is in the order: tertiary > secondary > primary. An anionic extracting system used extensively in laboratories and industry consists of triisooctyl amine (TIOA) in xylene/ toluene. 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 consists 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 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 +4 and VI are exchanged onto cation-exchange resins. Uranium (+4) is more strongly exchanged, and separation of U(VI) (UO_2^{+2}) is limited. On some cation-exchange columns, the ion also tends to tail into other ion fractions during elution. Exchange increases with temperature, however, and increasing the pH also increases exchange up to the beginning of formation of hydrolytic precipitates at pH 3.8. In strong acid solutions, U(VI) is weakly absorbed compared to uranium (+3 and +4) cations. Using complexing agents can increase specificity by elution of U(VI) with common complex-forming anions, such as chloride, fluoride, nitrate, carbonate, and sulfate.

Specificity also may be enhanced 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 U(VI) from other metals using the first method is to absorb U(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 U(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), the effect of pH on formation of complexes, and the net charge of the column are all variables controlling the separation process.

A number of chromatographic systems are available for uranium separation on anion-exchange resins. In hydrochloric acid, uranium is often exchanged and other cations are not. Uranium(VI) can be exchanged 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 exchanged on the column, and uranium is eluted exclusively with dilute hydrochloric acid. Various oxidation states provide another method of separation. U^{+4} is separated from Pr^{+4} and Th^{+4} with 8 M hydrochloric acid. Thorium, plutonium, zirconium, neptunium, and uranium can be separated individually by exchanging all the ions except thorium from concentrated hydrochloric acid. Plutonium (+3) elutes with concentrated acid, zirconium at 7.5 M, Np^{+4} with 6 M hydrochloric acid and 5 percent hydroxylamine hydrochloride, and uranium at 0.1 M acid. U^{+4} can be separated from U(VI) because both strongly exchangefrom concentrated hydrochloric acid, but they separate at 6 M acid because U^{+4} is not exchanged at that concentration. Uranium(VI) exchanges strongly on an anion-exchange resin in dilute hydrofluoric acid, and the exchange decreases with increasing acid concentration. Nitric acid provides an excellent method to purify uranium, because uranium is more strongly exchanged from nitric acid/nitrate solutions than from chloride/HCl solutions. More selectivity is achieved when acid concentration is low and nitrate concentrations are high. Exchange is greatest when aluminum nitrate is use as the source of nitrate. Ethyl alcohol increases exchange 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, U(VI) is electroplated on a platinum electrode from the basic solution adjacent to the

cathode that exists 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

Uranium may be determined by fluorimetry. During the separation and purification process, the sample is 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. Another technique related to fluorescence is kinetic phosphorimetry analysis (KPA). Aqueous solutions of the fully digested sample are exposed to a laser at a specific wavelength, and the phosphorescence (at a different wavelength) intensity is measured.

Total uranium may be determined by gross alpha analysis. Individual radionuclides of uranium, ^{234}U, ^{235}U, and ^{238}U, can be determined by their alpha-particle emissions. Mass spectrometry also can be used for longer-lived isotopes of uranium. 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 electrodeposition on a platinum or stainless-steel disc. In each of these techniques, care must be taken to ensure that a single oxidation state is achieved for the uranium prior to the collection technique. 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.

Neutron activation analysis (NAA) 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 absolute activation techniques using the Savannah River Reactor Activation Facility. NAA, followed by delayed-neutron detection, was commonly used to determine ^{235}U.

Compiled from: Alfassi, 1990; Allard et al., 1984; Ahrland, 1986; Baes and Mesmer, 1976; ASTM D5174; Bard, 1985; Booman and Rein, 1962; Choppin et al., 1995; Considine and

Considine, 1983; Cotton and Wilkinson, 1988; CRC, 1998-99; DOE, 1990 and 1997; Echo
and Turk, 1957; EPA, 1973; Ehmann and Vance, 1991; Fritz and Weigel, 1995; Greenwood
and Earnshaw, 1984; Grindler, 1962; Hampel, 1968; Hassinsky and Adloff, 1965; Hochel,
1979; Katz et al., 1986; Katzin, 1986; SCA, 2001; Weigel, 1986.

14.10.9.16 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 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. 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. Zirconium-
95 ($t_{1/2} \approx 64.0$ d) and ^{97}Zr ($t_{1/2} \approx 16.9$ h) are fission products and are beta emitters. Zirconium-93
($t_{1/2} \approx 1.53 \times 10^6$ 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, ilemenite, 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, along 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.

Zirconium-95 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:

$$^{90}_{38}Sr \rightarrow {}^{90}_{39}Y + \beta \rightarrow {}^{90}_{40}Zr + \beta$$
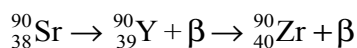
Zirconium metal and its alloys are highly resistant to corrosion and withstand streams of heated water under high pressure. These properties, along with their low cross section for thermal neutrons, make them an important material for cladding uranium fuel elements and as core armor material in nuclear 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. Zirconium-95 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/cm³. It exists 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 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 individuals 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. 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 form 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 the 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 with analyses of other radionuclides. 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 $Zr(SO_4)_3^2$. 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, 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. As the Zr^{+4} concentration increases and the concentration of H^{+1} decreases, however, hydrolysis and polymerization occurs, and one or more polymeric species dominates in solution. Amorphous hydrous oxides are precipitated near pH 2; they are soluble at high pH. Because of hydrolysis, soluble salts (nitrate, sulfate, perchlorate, acetate, and halides) form acidic solutions when they

dissolve. The reaction essentially seems to be a direct conversion to the tetranuclear $Zr_4(OH)_8(H_2O)_{16}^{+8}$ 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 Zr^{+4} 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. Because 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," on page 14-194, 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. 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. TBP is an excellent solvent for zirconium. It is used pure or with several nonpolar diluents, such as ethers, xylene/toluene, or carbon tetrachloride. Extractability increases with acid strength. A 0.01 M solution of tri-*n*-octylphosphine oxide (TOPO) in cyclohexane has been used to separate zirconium from 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 tracer 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 used to separate zirconium from such metals.

ION-EXCHANGE CHROMATOGRAPHY. Zirconium can be separated from 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 exchange 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 HCl. Fluoride complexes of zirconium and hafnium can be separated from other noncomplexing cations, because the negative complex ions are not exchanged, and the noncomplexing 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 from 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

Zirconium-95 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.

14.10.9.17 Progeny of Uranium and Thorium

The analysis of uranium and thorium isotopes is most frequently performed by alpha spectroscopic, liquid scintillation, mass spectrometry, or proportional-counting analysis. The analyst frequently is focused on the uranium and thorium analytes and can readily forget that the progeny of these isotopes also are radioactive. In fact, the decay chains may contain 10 to 14 different isotopes that all decay by beta or alpha emission. The radioactive progeny are analytes of importance in their own right. Thus, the analytical focus could be on the parent isotopes or on any of these progeny. It is important not to lose sight of the fact that even after separations the radioactive decay process continues, and new progeny are formed.

The elements that interfere most (due to their activities) with analysis of transuranics are radium, radon, actinium, lead, bismuth, and polonium. Radium, radon, and actinium form a group based on the decay of their isotopes and the relative half-lives of those isotopes. Lead, polonium, and bismuth form a "group," which are discussed separately as "contaminants" in the analysis of the transuranics or radium. There are specific analytical schemes for each of these that are developed in separate references.

Radium and Radon

Naturally occurring uranium and thorium give rise to the following principal radioisotopes of radium and radon:

$$^{238}U \xrightarrow{\alpha} {}^{234}Th \xrightarrow{\beta} {}^{234}Pa \xrightarrow{\beta} {}^{234}U \xrightarrow{\alpha} {}^{230}Th \xrightarrow{\alpha} {}^{226}Ra \xrightarrow{\alpha} {}^{222}Rn \qquad \text{[U-1]}$$

$$^{232}Th \xrightarrow{\alpha} {}^{228}Ra \xrightarrow{\beta} {}^{228}Ac \xrightarrow{\beta} {}^{228}Th \xrightarrow{\alpha} {}^{224}Ra \xrightarrow{\alpha} {}^{220}Rn \qquad \text{[Th-1]}$$
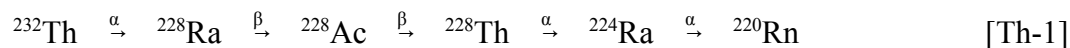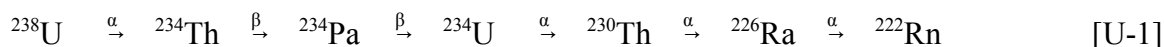
The presence of these isotopes in natural waters, soils, and buildings poses a level of radiological risk from exposure to gross alpha and beta emitters, which can result from diffusion of the radon gas or radium solubility. The primordial radium and radon atoms have long since decayed, so both elements now result from the decay of uranium and thorium.

If these decay chains were unaffected by the environment, secular equilibrium (Attachment 14A, "Radioactive Decay and Equilibrium") of uranium, thorium, and all their respective progeny would have occurred millions of years ago. This would mean that the analysis of the whole decay

chain could be performed by measuring one radionuclide's activity and using the Bateman equations to calculate the other activities. However, the noble gas chemistry of radon and the differential solubility of the other isotopes cause these chains to be disrupted or "broken." The latter part of the decay chain contains the isotopes of polonium, bismuth, and lead and are sometimes separately identified due to the break in the chain at radon.

Radon is an indoor exposure hazard because it can seep through barriers, such as concrete foundations. It will form its own radiochemical chain from its decay as parent to isotopes of the polonium/bismuth/lead group:

[Rn-1]

$$^{222}Rn \xrightarrow{\alpha} {}^{218}Po \xrightarrow{\alpha} {}^{214}Pb \xrightarrow{\beta} {}^{214}Bi \xrightarrow{\beta} {}^{214}Po \xrightarrow{\alpha} {}^{210}Pb \xrightarrow{\beta} {}^{210}B \xrightarrow{\beta} {}^{210}Po \xrightarrow{\alpha} {}^{206}Pb$$

$$^{220}Rn \xrightarrow{\alpha} {}^{216}Po \xrightarrow{\alpha} {}^{212}Pb \xrightarrow{\beta} {}^{212}Bi \xrightarrow{\beta} {}^{212}Po \xrightarrow{\alpha} {}^{208}Pb$$

[Rn-2]
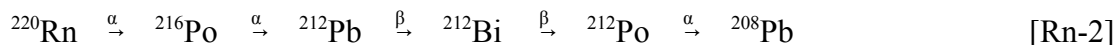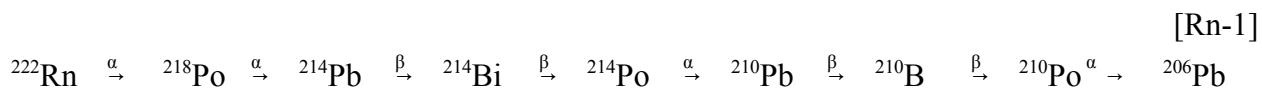
The inert characteristic of the radon allows it to transport radioactivity to locations distant from the source. With chemical characteristics similar to calcium, however, radium will be similarly mobile in ground water. Thus, the analysis of radium and radon and their isotopes generally is done separately.

The chemistry of radium is detailed in Section 14.10.9.9. Direct analysis by the methods described will be satisfactory for large amounts of the material. The activity of radium found in many environmental or low activity samples represents an analytical challenge. The half-lives of the radium isotopes are quite long ($^{228}Ra \approx 5.8$ y; $^{226}Ra \approx 1,600$ y). Thus, long counting times or very large samples are needed to achieve statistically relevant values at the minimum detectable level needed to meet regulatory requirements. Analytical methods have been developed to perform this task but suffer from large statistical error and from the handling of large samples. To circumvent these difficulties, indirect analytical techniques have been developed for each of these isotopes that rely on the chemistry of radium to obtain radiochemical purity, and on the Bateman equation of parent-progeny relationships to produce the shorter-lived progeny. The parent activity is determined by mathematical analysis from the progeny activity.

An example is in the analysis of ^{226}Ra. Radium is isolated by coprecipitation with barium as the sulfate. The precipitate is then dissolved according to the following:

$$Ba/RaSO_4 \xrightarrow{EDTA} Ra/Ba(EDTA)^{-2}$$

[Rn-3]

The solution of radium complex is immediately transferred to a vessel (called a de-emanation tube) that is sealed under vacuum. This is a key aspect of the process, because the principal decay product is a noble gas. The decay of radium occurs according to [U-1] and [Th-1] above. According to the Bateman equations, after approximately 21 days, full equilibrium is established

for [Rn-1]. Equilibrium for [Rn-2] is achieved in about 2 days. At the end of the equilibration period, the de-emanation tube is purged slowly with helium into a calibrated phosphorescence cell for counting. This removes the noble gas from all its progeny and parents, which are non-volatile. This time, however, equilibration is much shorter (on the order of four hours), and the analysis includes all of the progeny isotope emanations as well as those of the parents. The analysis for ^{222}Rn may have to be corrected for ^{220}Rn presence if thorium was a major contributor to the transuranic composition of the sample.

The remnant solution is used for the analysis of ^{228}Ra by exploiting the rapid achievement of secular equilibrium (already achieved) with its daughter isotope, ^{228}Ac, which is not volatilized during the nitrogen purge.

The radium isotopes again are removed by coprecipitation with barium as sulfates, but this time redissolved by diethylene triamine pentaacetic acid (DTPA).

$$ (Ba/Ra)SO_4 \quad \overset{DTPA}{\rightarrow} \quad [(Ba/Ra)(DTPA)]^{-3} \quad \overset{20\% \; Na_2SO_4}{\rightarrow} \quad (Ba/Ra)SO4 \quad \overset{DTPA}{\rightarrow} \quad [(Ba/Ra)(DTPA)]^{-3} \quad [Rn-4] $$
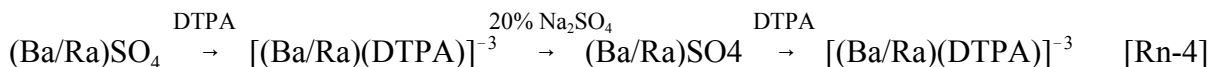
This is used to remove any residual ^{228}Ac. The solution of the DTPA complex is stored for a set period of time (usually about 36 hours), and the radium parent is removed by precipitation. The supernatant solution contains the actinium daughter. At the time of the separation, the actinium and radium activities are equal (see Attachment 14A, "Radioactive Decay and Equilibrium"). The activity of the actinium is determined and back-corrected to determine the radium activity.

Lead, Polonium, and Bismuth

Differential solubility and radon volatility play an important part of the spread of these naturally occurring radioisotopes in the environment. Looking at [Rn-1], the three most significant isotopes in this group are ^{210}Pb, ^{210}Bi, and ^{210}Po because of their half-lives. In [Rn-2], the significant isotope is ^{212}Pb, also because of its half-life. Both of these end-of-the-chain series can present problems in environmental analyses.

The purpose of the gross analysis is to be able to use a single, simple analysis as part of the decision process for requiring more complex analysis and dose estimation. The problem with gross alpha analysis, especially at the environmental level, is that it is subject to many sources of error. The most significant source of these errors has been shown to be the time between sample collection and analysis. In this case, elevated alpha activity was not attributed to $^{226/228}$Ra, but instead to ^{224}Ra. Radium-224, its short-lived decay-chain progeny including ^{212}Pb ($t_{1/2} \approx 10.6$ h), ^{212}Bi ($t_{1/2} \approx 1$ h), and ^{212}Po ($t_{1/2} \ll 1$ sec), were causing the variation in the activity. If the samples were counted too long after acquisition, gross alpha would be high due to the buildup of the short-lived progeny. Because the half-lives were measured in hours, a consistent time-after-sample needed to be established to standardize the buildup of the short-lived isotopes

Similarly, trying to account for the activity from alpha/beta emitters from the [Rn-1] chain is difficult because ^{210}Pb (t$_{1/2} \approx$ 22.6 y) emits very low-energy beta particles and gamma rays and quickly reaches equilibrium with its bismuth and polonium progeny. An analysis for ^{210}Pb has been developed that is specific and sensitive. The lead present in the sample is chemically separated from the bismuth by precipitation. The bismuth is removed by washing, and only the bismuth produced by the lead decay is measured. This relies on the secular equilibrium established by ^{210}Pb/^{210}Bi after separation of the lead (Attachment 14A, "Radioactive Decay and Equilibrium"). The ingrowth of bismuth is allowed, and complexation and precipitation remove the parent, lead. Yield is determined by the addition of bismuth carrier after the ingrowth period.

The scheme is outlined here.

$$\text{Sample} \xrightarrow{\text{Ba Carrier} + \text{H}_2\text{SO}_4} \text{(Ba/Pb)SO}_4 \xrightarrow{\text{pH 4/EDTA}} [(\text{Pb})(\text{EDTA})]^{-2}_{aq} \xrightarrow{\text{pH 1/H}_2\text{SO}_4} \text{PbSO}_4 \downarrow \xrightarrow{\text{Na}_2\text{CO}_3} \text{PbCO}_3 \downarrow \rightarrow$$
$$\text{(ingrowth begins)}$$

$$\xrightarrow{\text{HCl} + \text{Bi carrier}} \text{BiOCl} \downarrow + \text{Pb}^{+2}$$
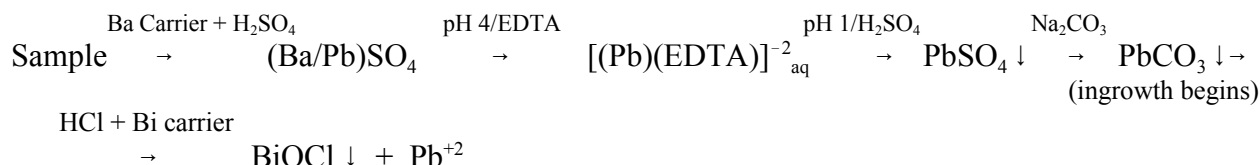
This represents a special exception to adding carrier. Usually, it is added at the beginning of the analysis. However, in this case, the bismuth carrier would have brought nonequilibrium bismuth through the analysis, creating an inaccuracy. Thus, adding the bismuth carrier at the end ensures maximum recovery of only the newly formed isotope.

Compiled from: Bagnall, 1957; EPA, 2000; Parsa, 1998; To, 1993.

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ATTACHMENT 14A
Radioactive Decay and Equilibrium

The rate of decay of a number of atoms, N_1, of a radionuclide can be expressed by Equation 14A.1, where λ_1 is $(\ln 2)/t_{1/2}$ for the radionuclide and t is the time during which the change in N_1 is observed:

$$-\left(\frac{dN_1}{dt}\right) = \lambda_1 N_1 \qquad (14A.1)$$

The radionuclide may decay to a stable nuclide, or to another radionuclide. In the first instance, the total number of atoms of stable nuclide formed as a result of the decay of N_1 eventually will equal N_1.

When the decay product of the original radionuclide is another radionuclide, three distinct equilibrium relationships exist between the parent and progeny based on the half-lives of the original and newly formed radionuclides. "Radioactive equilibrium" may be described mathematically by combining the decay-rate equations of two or more radionuclides to relate the number of atoms of one to any of the others. The three relationships between parent and progeny are referred to as "secular," "transient," and "no equilibrium" (Friedlander et al., 1981).

14A.1 Radioactive Equilibrium

A dynamic condition is initiated when a parent decays to a radioactive progeny. The progeny has its own decay equation, analogous to Equation 14A.1:

$$-\left(\frac{dN_2}{dt}\right) = \lambda_2 N_2 \qquad (14A.2)$$

The relationships may become complicated if the progeny gives rise to an isotope that is also radioactive. In this case, the relationship would become, "parent–1st progeny–2nd progeny." This connection of the radionuclides is referred to as a radioactive "decay chain." When the parent of the chain is present, some number of atoms of all of the progeny in the chain eventually will be present as the predecessor radionuclides undergo radioactive decay.

14A.1.1   Secular Equilibrium

Secular equilibrium occurs when half-life of the progeny is much less than the half-life of the parent. An example, using the parent-progeny relationship between ^{210}Pb ($t_{1/2} \approx 22.6$ y) and ^{210}Bi ($t_{1/2} \approx 5$ d), can be used to demonstrate this case. (For illustrative purposes, ignore the radioactive progeny of the ^{210}Bi radionuclides).

Figure 14A.1 identifies the entire decay chain from ^{238}U, of which ^{210}Pb and ^{210}Bi are a part.
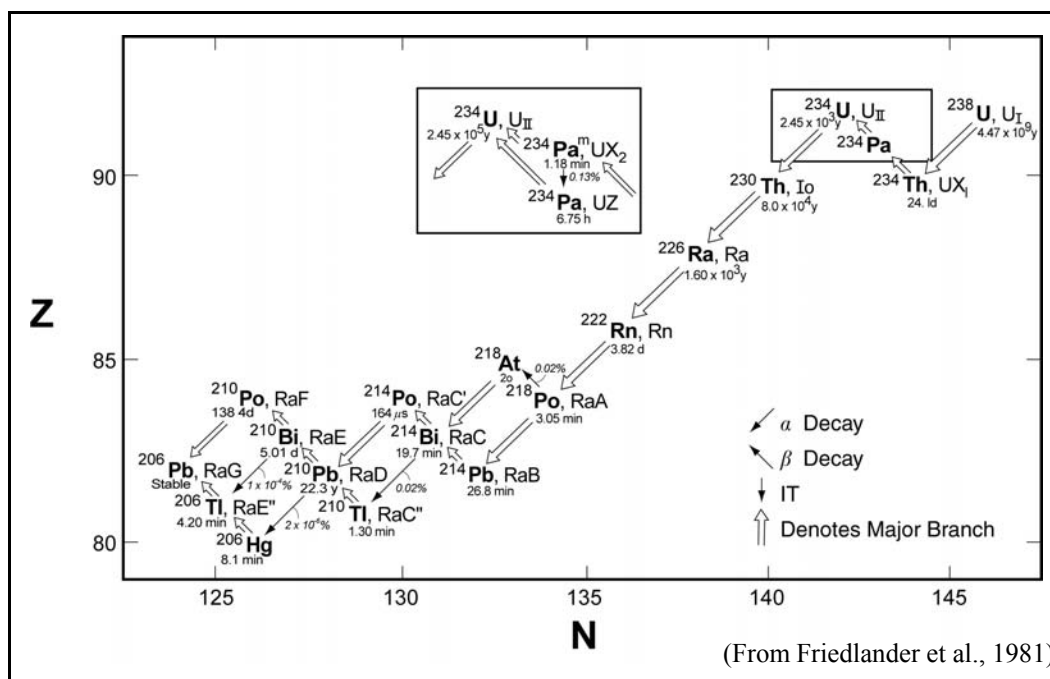
FIGURE 14A.1 — Decay chain for ^{238}U

When a group of atoms of lead are isolated (e.g., radiochemical purity is achieved by precipitation), no atoms of bismuth are present at the time of isolation (t = 0). From that moment, the number of atoms of bismuth present can be described by two equations: the rate of decay of the lead and the rate of decay of the bismuth. For each atom of lead that decays, one atom of bismuth is produced. Thus a single equation can be developed to show this relationship:

$$\text{Activity of } ^{210}\text{Bi} = \left[\frac{dN_2}{dt}\right] = \lambda_1 N_1 - \lambda_2 N_2 \qquad (14A.3)$$

This equation can be solved to yield a relationship between the number of atoms of lead and bismuth at any time *t* after the isolation of lead. The general equation is:

$$N_2 = N_1^0 \left[\lambda_1/(\lambda_2 - \lambda_1)\right]\{e^{-\lambda_1 t} - e^{-\lambda_2 t}\} + N_2^0 \, e^{-\lambda_2 t} \qquad (14A.4)$$

Where: N_2 = atoms of progeny (bismuth), present at any time *t*
N_1^0 = atoms of parent (lead), initially present
λ_1 = decay constant of parent
λ_2 = decay constant of progeny

N_2^0 = The number of atoms of progeny present at the time of isolation of parent.

The activity of the progeny (A_2) can then be calculated by multiplying both sides of Equation 14A.4 by λ_2:

$$A_2 = \lambda_2\, N_2 = N_1^0\, [\lambda_2\, \lambda_1/(\lambda_2 - \lambda_1)]\{\, e^{-\lambda_1 t} - e^{-\lambda_2 t}\,\} + \lambda_2\, N_2^0\, e^{-\lambda_2 t} \qquad (14A.5)$$

If radiochemical purity is ensured initially, then

$$N_2^0 = 0 \qquad (14A.6)$$

and the terms including N_2^0 in both Equations 14A.4 and 14A.5 equal zero.

Plotting this relationship as a function of time yields the graph shown in Figure 14A.2 for the ^{210}Pb-^{210}Bi radionuclides. The three significant aspects of this relationship are:

- The total activity of the sample actually increases to a maximum (until it is $\approx 2A_{Pb}$),

- The activity of the bismuth and lead are approximately equal after about seven times the half-life of bismuth, and

- The activity of bismuth decays with the half-life of lead after equilibrium has been established.
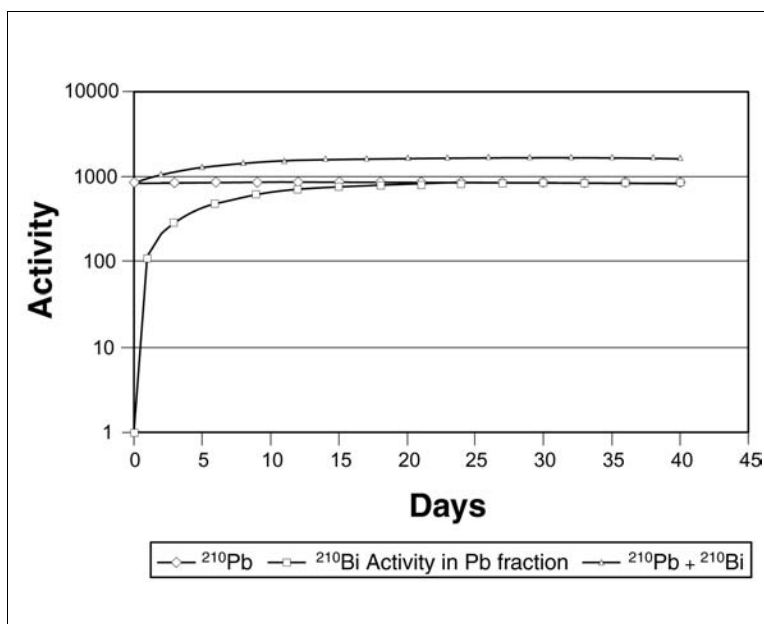
FIGURE 14A.2 — Secular equilibrium of ^{210}Pb/^{210}Bi

14A.1.2   Transient Equilibrium

Transient equilibrium occurs when the half-life of the progeny is less than the half-life of the parent. This can be demonstrated using the relationship between ^{95}Zr ($t_{1/2} \approx 64$ d) and ^{95}Nb ($t_{1/2} \approx 35$ d). Figure 14A.3 identifies the same types of relationships as were seen in the case of secular equilibrium. For transient equilibrium, the total activity passes through a maximum, and then decreases with the characteristic half-life of zirconium. Note that the activity of the niobium exceeds the activity of the zirconium after about 2 half-lives of the niobium. A significant aspect

of this radioactive equilibrium that occurs at about this time is that the activity curve for the progeny reaches a maximum value. This can be determined for the general case by taking the first derivative of Equation 14A.5 and setting it equal to zero (Equation 14A.7):

$$A_{\text{maximum, progeny}} = \frac{[\lambda_1 - \lambda_2]}{[\ln \lambda_1 - \ln \lambda_2]}$$

(14A.7)
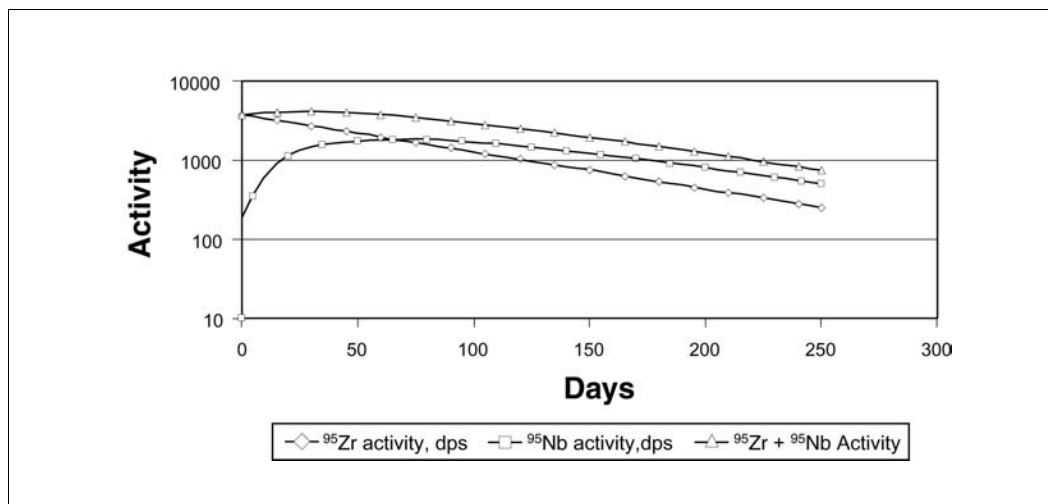
FIGURE 14A.3 — Transient equilibrium of ^{95}Zr/^{95}Nb

For the example in Figure 14A.3, this occurs at 67 days. When performing low-level analysis, knowing when this maximum activity occurs can help to achieve a lower minimum detectable amount of the progeny.

After approximately seven times the half-life of the progeny (in this case ^{95}Nb), the activity of the progeny decays with the half-life of the parent, similar to the secular equilibrium case. If the ^{95}Nb were to be separated from the parent at any time, it would decay with its own characteristic half-life.

14A.1.3   No Equilibrium

The no-equilibrium case occurs when the half-life of the progeny is greater than the half-life of the parent. Figure 14A.4 demonstrates this example for ^{239}U ($t_{1/2} \approx 23.5$ min) and ^{239}Np ($t_{1/2} \approx 2.36$ d $\approx 3,400$ min). The notable characteristic here is the total activity continually decreases after time zero.
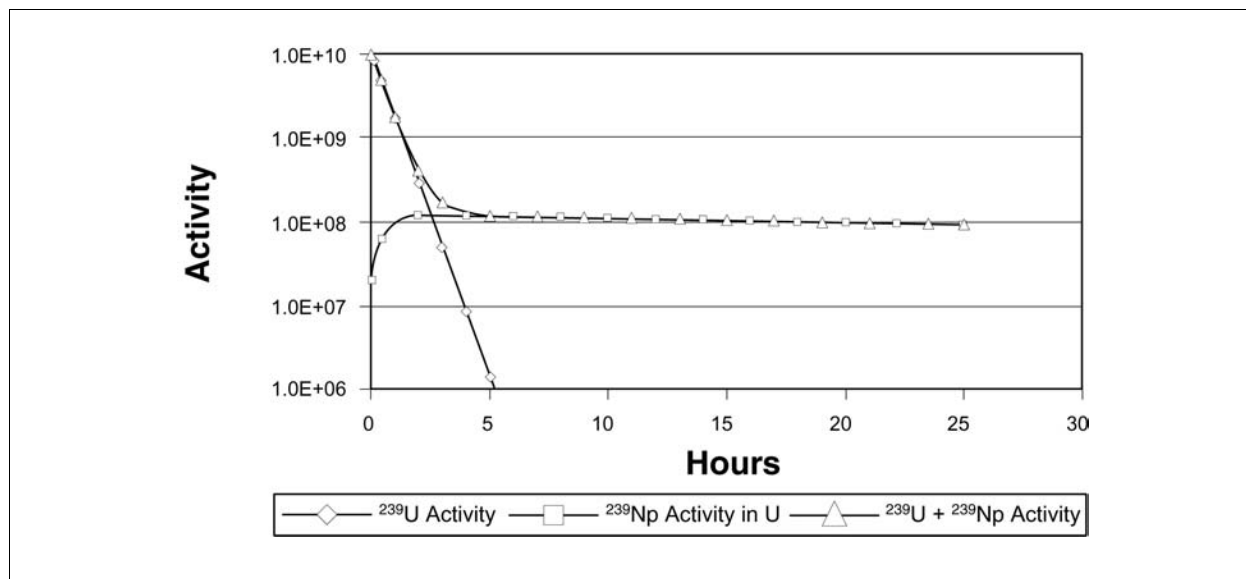
FIGURE 14A.4 — No equilibrium of ^{239}U/^{239}Np

14A.1.4   Summary of Radioactive Equilibria

In all three cases, Equation 14A.5 is used to calculate the activity of progeny after radiochemical separation of the parent. The important aspects of the relationship (Table 14A.1) are:

- It allows the analyst to optimize when, and for how long, to count a sample in which a parent-progeny relationship exists. For the secular and transient radiochemical equilibria, if approximately seven times the half-life of the progeny has passed, then equilibrium has been established. Thus for the ^{90}Sr/Y parent-progeny pair, the time to reach maximum activity is $\approx 7 \times (t_{\frac{1}{2}\ Yttrium})$, or about 18 days.

- For the "transient equilibrium" case, a higher progeny activity may be achieved (relative to the parent), thus improving counting statistics for calculation of the initial parent activity.

- For the "no-equilibrium" case, if approximately seven times the half-life of the parent has passed, only progeny is left, and the activity of progeny can be related directly to the initial activity of the parent.

- It provides the analyst with important information about timing of intermediate separation steps in procedures (e.g., whether or not analysis must proceed immediately or can be set aside for a certain period of time).

TABLE 14A.1 — Relationships of radioactive equilibria

Type of Equilibrium	Relationship of Half-lives	Advantages	Other Useful Examples
Secular	Parent >> Progeny	If progeny half-life is as short as a few days, equilibrium is established in a reasonable time frame for analysis.	^{90}Sr – ^{90}Y ^{137}Cs – ^{137m}Ba ^{226}Ra – ^{222}Rn ^{228}Ra – ^{228}Ac
Transient	Parent > Progeny	If both half-lives are measured in hours to days, equilibrium activity of progeny peaks in a reasonable time frame for analysis.	^{222}Rn with its decay chain (for de-emanation analysis) ^{212}Pb – ^{212}Bi
None	Parent < Progeny	If parent half-life is a day or less, its activity contributes negligibly after a week.	^{131}Te – ^{131}I

14A.1.5   Supported and Unsupported Radioactive Equilibria

The connection between parent and progeny has one additional aspect that is significant for environmental analysis: whether or not the progeny activity is constantly "supported" by the parent in the sample. When the progeny is constantly supported, it appears to have the half-life of the parent. However, it can become unsupported, in which case it would decay with its own characteristic half-life.

For example, consider a soil sample that was contaminated with 3.7 Bq/g (100 pCi/g) of ^{232}Th ($t_{1/2} \approx .4 \times 10^{10}$ y). One concern about this radionuclide is the dissolution of some of its progeny into ground water: ^{228}Ra ($t_{1/2} \approx 5.76$ y), ^{224}Ra ($t_{1/2} \approx 3.66$ d) and ^{220}Ra ($t_{1/2} \approx 55.6$ s). Ground-water pH is normally between 6 and 8. At this pH, and with the crustal concentration of thorium/ radium, the solubility of radium is significantly greater than that of thorium. As ^{228}Ra dissolves in the ground water, the ^{232}Th parent remains in the soil phase. The ground water will then migrate with the radium into wells, streams, aquifers, etc. The radium in the ground water is now "unsupported" because it is no longer in equilibrium with the decay of the thorium.

If we continue to follow the decay chain to ^{228}Th, the insolubility of thorium again "breaks" the decay chain in the ground water, because it will precipitate. However, its two progeny (^{224}Ra and ^{220}Rn) will continue to be soluble, and thus also be unsupported.

This is important when making decisions about sample shipment method and holding times prior to analytical separations. If it is assumed that the decay chain is supported, there is no reason to hasten the onset of the chemical analysis. However in the unsupported case, the half-lives of the ^{224}Ra and ^{220}Ra will affect the ability to achieve project measurement quality objectives and data quality objectives.

14A.2 Effects of Radioactive Equilibria on Measurement Uncertainty

14A.2.1   Issue

It is sometimes necessary to ensure that radionuclides have achieved radioactive equilibrium with their progeny or to establish and correct for disequilibrium conditions. This is particularly applicable for protocols that involve the chemical separation of long-lived radionuclides from their progeny, or long-lived progeny from their parents. This is also applicable for nondestructive assays like gamma spectrometry, where photon emission from progeny may be used to determine the concentration of a stable parent, or a parent which is radioactive but not a gamma emitter.

14A.2.2   Discussion

Application of Equations 14A.4, 14A.5, 14A.6 and 14A.7 can be shown by example. Radium-226 ($t_{1/2} \approx 1,600$ y), is a common, naturally occurring radionuclide in the uranium series. Radium-226 is found in water and soil, typically in secular equilibrium with a series of shorter-lived radionuclides beginning with the ^{222}Ra ($t_{1/2} \approx 3.8$ d) and ending 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 re-accumulate. 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 analysis of radon is performed, the ingrowth of all progeny must be allowed prior to counting in order to minimize uncertainty. Examining the decay chain (Figure 14A.1) and the respective half-lives of radionuclides through ^{214}Po (for the purposes of the analysis, the progeny ^{214}Pb ends the decay chain and contributes insignificantly to the total count rate), it is appropriate to wait about 3 or 4 hours. 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.

Radioactive 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 length of time between separation of parent and progeny.

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 ratios. Data from analysis of ores or materials involved in processing that

could disrupt naturally occurring relationships (i.e., selectively remove elements from the material) require close attention in this regard.

All numerical methods (electronic and manual) should be evaluated to determine if the appropriate correction factors related to equilibrium concerns have been used. 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). A specific example is ^{228}Ra analysis with ingrowth of ^{228}Ac. The actinium is separated from the radium after a measured time and is immediately counted. The half-life of actinium is used to correct for the decay of actinium atoms during the counting interval and for the time interval since the separation from radium. Equation 14A.4 is used to calculate the atoms of radium, based on the number of atoms of actinium, at the time of separation of actinium from radium. The half-life of radium is used to calculate the radium activity and decay-correct from the sample preparation time back to the time of sample collection as follows:

$$N_B = N_c/[\varepsilon][1\text{-}EXP(\text{-}\lambda_{Ac}t_c)]$$

and

$$N_0 = N_B \{EXP(\text{+}\lambda_{Ac}t_s)\}$$

Where:
　　N_c is the number of counts accumulated during the counting interval
　　N_B is the number of atoms of actinium at the beginning instant of the count interval
　　N_0 is the number of atoms of actinium decay corrected back to the time of separation from Ra
　　λ_{Ac} is the decay constant for actinium
　　ε is the detector efficiency
　　t_c is the counting interval (clock time)
　　t_s is the time between separation of actinium from radium to the start of the count interval.

Equation 14A.4 is then used to calculate the atoms of radium based on the number of atoms of actinium that exist at the time actinium is separated from radium. The half-life of radium is used to calculate the radium activity and decay-correct from the sample preparation time back to the time of sample collection.

Samples requiring progeny ingrowth should be held for sufficient time before counting to establish 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 minimum detectible concentration or adversely affect the measurement uncertainty.

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.

14A.2.3   Examples of Isotopic Distribution – Natural, Enriched, and Depleted Uranium

Isotopic distribution is particularly important with respect to uranium, which is ubiquitous in soils and is 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[2], i.e., uranium as found in nature (Parrington et al., 1996). The ratio of ^{238}U to ^{234}U in undisturbed uranium deposits will be the same as the ratio of $99.2745/0.0055 = 18,050$, because all the ^{234}U comes from the decay of ^{238}U (^{234}U originally present when the Earth was formed has long since decayed).

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 produces material that is called "DU," or depleted in uranium (i.e., the uranium from which the ^{235}U was taken[3]). The enrichment process also will disrupt the ^{234}U content, which will change the $^{238/234}$U ratio from what is occurring naturally (i.e., 18,050). 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 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 that are time- and cost-intensive, but which provide the material's definitive isotopic distribution. It is often

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

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

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.

14A.3 References

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15 Quantification of Radionuclides

15.1 Introduction

This chapter presents descriptions of counting techniques, instrument calibration, source preparations, and the instrumentation associated with these techniques, which will help determine what radioanalytical measurement methods best suit a given need. This chapter also describes radioanalytical methods based on nuclear-decay emissions and special techniques specific to the element being analyzed. 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, samples may require quantitative identification of many radionuclides for which the laboratory may need to prepare unique calibration sources. In the latter case, specialized instruments are available. Typically, a radiochemical laboratory routinely will encounter samples that require a level of information between these two extremes.

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*). This chapter focuses on the instruments used to detect the radiations from the isolated radionuclides or the atoms from the separations and purification processes.

A typical laboratory may be equipped with the following nuclear counting instrumentation:

- Gas proportional detectors for alpha and beta-particle counting (GP);

- Sodium iodide or high resolution germanium detectors for gamma detection and spectrometry [NaI(Tl) and HPGe];

- Low-energy gamma- or X-ray detectors [HPGe or Si(Li)];

- Solid-state detectors for alpha spectrometry (HPGe); and

Contents

- Liquid scintillation counters suitable for both alpha- or beta-emitting radionuclides (LSC and "Photon Electron Rejecting Alpha Liquid Scintillation"—PERALS®).

It may also have the following equipment, which rely on atom- or ion-counting techniques, molecular methods of analysis, or gamma-ray spectrometry:

- Kinetic Phosphorimeter Analysis (KPA)
- Mass Spectrometric Analyses
    - Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)
    - Thermal Ionization Mass Spectrometry (TIMS)
    - Accelerator Mass Spectrometry (AMS)
- Neutron Activation

15.2 Instrument Calibrations

In this chapter, the term "test source" is used to describe the radioactive material prepared to be introduced into a measurement instrument, and "laboratory sample" is 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" means that the prepared source is for calibrating instruments.

The goal of calibration- or test-source preparations is to maximize detection capability while minimizing the introduction of bias and uncertainty into the measurement process. To achieve this goal, calibration sources should be prepared in a manner that provide comparability to test sources with respect to geometry, composition, and distribution of the test-source material within a container or on a source mount. This section will provide an overview of the need for calibration and test-source-correspondence congruence, analyte homogeneity within the source, corrections for self-absorption and scattering of the emitted radiations, and estimation of calibration uncertainty. Specific information and guidance relative to these topics can be found in the subsequent sections of this chapter and in Chapters 13, 14, 19, and 20.

Proper instrument calibrations are essential for the proper identification and quantification of radionuclides in samples. It is important to initially calibrate the instruments with calibration sources that are traceable to a national standards body. Once calibrated, the continuing validity of calibrations should be checked on a periodic basis (Chapter 18, *Laboratory Quality Control*) as specified in a laboratory's quality manual. This is usually done by counting a check source or some secondary calibration source 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 and laboratory quality documents (Chapter 4, *Project Plan Documents*) and in analytical statements of work

(Chapter 5, *Obtaining Laboratory Services*). Section 18.5.6 ("Summary Guidance on Instrument Calibration, Background, and Quality Control") within Chapter18 provide guidance on the frequency of instrument calibration and quality controls checks when requirements are not specified in a statement of work.

15.2.1 Calibration Standards

Instrument calibration should be performed as needed only with sources traceable to a national standards body such as the National Institute of Science and Technology (NIST) in the United States (ANSI N42.23). Calibrations of instruments should be made using certified reference materials of known and documented value and stated uncertainty. These certified reference materials may be supplied by:

- NIST (www.nist.gov) and the New Brunswick Laboratory (www.nbl.doe.gov) directly;

- A calibration-source supplier whose measurement capabilities or manufacturing processes are tested periodically by NIST (complies with ANSI N42.22);

- International Atomic Energy Agency (www.www.iaea.org/programmes/aqcs/main_database. htm);

- Other national standards bodies such as the National Physics Laboratory (NPL) of the United Kingdom (www.npl.co.uk/) and Physikalisch-Technische bundesanstalt (PTB) of Germany (www.ptb.de/); or

- A calibration-source supplier who documents derived materials with stated uncertainty, and whose values has been verified with analytical and measurement systems that have been tested periodically through an unbroken chain of comparisons to the national standards.

The sections on alpha, beta, and gamma-ray detection methods have subsections (15.4, 15.5, and 15.6) that list the nuclides commonly used for instrument calibrations.

15.2.2 Congruence of Calibration and Test-Source Geometry

For nuclear-decay emission analyses, instrument calibrations generally are performed to establish the detector counting efficiency of an instrument. The detector counting efficiency establishes the rate of detected events registered in the detector(s) of a counting system compared to the particle- or photon-emission rate of the source. Counting efficiencies are specific to the radionuclide (emission type or energy), the geometrical relationship between the source and detector, and a number of characteristics of the source material, especially those that affect the 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 analytical requirements and the variety of media encountered.

Where the efficiency of the detector varies with energy, it may be necessary to perform the calibration at a number of energies and to establish an efficiency curve that covers the range of energies to be encountered. Some radiation detection instruments require other types of calibrations. These are discussed under specific instrument calibrations. Generic issues that govern the conduct of calibrations are discussed below, and specific instrument and test-source considerations are provided in the appropriate sections in this chapter.

To assure that the instrument calibration is unbiased, calibration sources should 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, should be controlled. Backscatter, scattering, and self-absorption present during test-source counting should 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, an alternate radionuclide may be selected that has the same type of particle or photon emission (α, β, or γ) and approximate energy. When calibrating an instrument in this manner, corrections should be made for any differences between the decay schemes of the two nuclides. Calibrations used in alternate radionuclides should be verified to produce satisfactory results.

If any factor could vary that would significantly affect the counting efficiency determination with respect to measurement quality objectives (MQOs), calibrations should be performed that 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 because of absorption in the variable source thickness.

The geometry of a test source should be suitable for the counting instrument and—particularly—it should be reproducible. The test-source geometry should remain constant from source to source and with respect to that of the calibration source. This requirement is necessary for performing accurate measurements of all types of radioactivity and for all types of measurement instruments.

15.2.3 Calibration and Test-Source Homogeneity

The calibration and test sources should be prepared in a manner that reduces the nonuniformity of the material. Any deviation from this requirement can lead to biased results and contribute to the overall uncertainty of the laboratory results. Source uniformity is related to the physical nature of the source material. Uniformity of 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 source material over its cross sectional area. If sources are deposited in a nonuniform manner, absorption characteristics will vary from source to source, and acceptable reproducibility may not be achieved.

Variation in 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 sources that are hygroscopic, once prepared, often are stored in a desiccator to maintain a constant moisture content. Source uniformity is relevant to gamma-ray measurements, not because of the absorption of gamma rays, but because nonuniformity (inhomogeneity) 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. Since measurements of nonuniform sources are not reproducible, radioactive sources of all types should be homogeneous.

Liquid sources are more likely to be homogeneous than are solids, particularly if a reference material has been added to a solid matrix, such as soil. Multiple-phase samples are some of the least homogeneous matrices. Precipitates and multiple-phase liquid samples cannot provide consistent results unless particular measures are taken to ensure their homogeneity (e.g., remove suspended solids, dissolve and recombine, or analyze separately). 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.

15.2.4 Self-Absorption, Attenuation, and Scattering Considerations for Source Preparations

Alpha and beta particles emitted from 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). Absorption and scattering within the source material are less pronounced when measuring gamma rays than when analyzing for charged particles.

In order to ensure accurate results, it is important that calibration sources for the determination of

counting efficiency and self-absorption corrections are prepared identically in all aspects to the expected test sources. 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, sources prepared for alpha-particle measurements should be very thin and uniform for maximum detection capability and reproducibility.

Because of their much smaller mass, beta particles are scattered more readily in the source material than alpha particles. Depending on counter geometry, the measured beta-particle count rate (from sources of equal activity) can increase first as the source thickness increases because of the scattering of electrons out of the source plane and into the detector (Friedlander et al., 1981). At greater thicknesses, self-absorption begins to dominate, and the observed count rate 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 0.75 R (Friedlander et al., 1981). A scattering/self-absorption factor can be used, however, to correct the measured count rate (or activity) at a given source mass 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 source material, and x is the source thickness (Friedlander et al., 1981).

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 source should be controlled. The following procedures are often followed in order to maintain a low and constant moisture content of sources to be counted.

- Sources prepared by precipitation or coprecipitation may be dried with the filter in the suction-filter apparatus by washing the precipitate with a volatile, nonaqueous solvent. Acetone or ethanol typically is used for this purpose. The filter with source is removed from the filtering apparatus, mounted on a planchet, and stored in a desiccator prior to counting. Alternatively, a wet precipitate on the filter paper may be dried under a heat lamp and mounted on a planchet. In some cases, the wet precipitate is transferred as a slurry to a planchet and dried under a heat lamp.

- Electroplated sources are dried by heating on a hot plate, in an oven, or under a heat lamp.

- Laboratory samples analyzed nondestructively usually are dried prior to measurement in order to control moisture content and help ensure that source characteristics are reproducible.

Laboratory samples, such as soil, biota, and vegetation, usually are dried in an oven. When an even moisture content is important, sources should be maintained in a desiccator.

• Evaporated sources may be flamed and then stored in a desiccator to maintain a constant moisture content.

Another concern in measuring both alpha and beta particles from deposited sources is back-scattering: the scattering of particles from the source mount back through the source material and into the sensitive part of the detector. Backscattered 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, but the percent of backscattered beta particles from the source should remain constant and be consistent with that of the calibration 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). Thus, to reduce the affect of backscatter on beta-particle measurements, the source often is mounted on a thin, low Z (atomic number), low density material, such as 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 because of 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). Therefore, because of the dependency of backscatter on atomic number and thickness, the backing used for the calibration source should be identical to that used for the source mount. For example, if the presence of hydrogen chloride in the source requires changing from an aluminum planchet to platinum, a platinum backing should also be used in counting the calibration source.

15.2.5 Calibration Uncertainty

There are many parameters that may affect the calibration of an instrument and subsequent test-source results. These parameters may include those associated with the calibration source (certified value and source purity), the source matrix/mount (nuclide and matrix homogeneity, self absorption and backscatter), and the measurement process (variability among calibration and test-source geometry/matrix, source-to-detector positioning, and counting uncertainty). Quantifying the uncertainty of each parameter during an instrument calibration is extremely important and a necessity for calculating realistic measurement uncertainties. The uncertainties (standard uncertainty) in the various parameters affecting the instrument calibration should be propagated to give a combined standard uncertainty (CSU). The CSU should be documented on the calibration certificate or report. A detailed discussion on the propagation of uncertainties applicable to calibration and test-source measurements can be found in Chapter 19. An instrument calibration certificate/document should include an estimate of the calibration

uncertainty.

The counting uncertainty associated with a 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, sufficient counts should be accumulated to obtain a 1 percent (1 standard deviation) or less net counting uncertainty when calibrating a detector system. 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 should be aware of the potential for detector contamination, this is particularly true for semiconductor detectors used for alpha spectrometry.

15.3   Methods of Source Preparation

This section provide an overview of various commonly used methods used to prepare calibration and test sources. Source preparation methods specific to the measurement of nuclear decay emissions (α, β, γ) and atoms or mass also may be found in Sections 15.4, 15.5, and 15.6. The source preparation categories in this section include electrodeposition, precipitation/coprecipitation, evaporation, thermal volatilization/sublimation, and special source matrices.

15.3.1 Electrodeposition

High-resolution alpha spectrometry requires a very thin, uniform, flat, and nearly massless source mount. Ideally, the source plate to determine alpha activity by a spectrometer would be a flat plate coated with a single layer 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). For certain long-lived nuclides, such as ^{232}Th, there may be micrograms of the plated nuclide that can affect the alpha spectrometry resolution.

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, serves as the anode of the cell. Deposition of actinides for alpha spectrometry also has been performed in disposable cells constructed from 20-30 mL polyethylene scintillation vials and highly polished stainless-steel planchets (Talvite, 1972). Disposal of the plastic cells

prevents cross contamination. The composition of the electrolyte and the parameters applied in the electrodeposition 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). 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 ethylene diamine tetraacetate, or 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, which interfere with the electrodeposition of plutonium and americium in his process. Cable et al. (1994) provide guidance on the optimum conditions for the electrodeposition of actinides, U, Th, Pa, Pu, and Am.

Electrodeposition is applicable to more than 30 radionuclides. The main advantage of electro-deposited sources over other methods of preparation is their extremely thin, uniform deposit of a radionuclide on a plate, which permits high resolution spectrometry; however, the yield is often not quantitative (Adloff and Guillaumont, 1993). Thus, the yield should be monitored with the inclusion of a known quantity of another radioisotope of the same element whenever feasible, which is deposited simultaneously with the analyte. Radioactive sources of the following elements have been prepared successfully by electrodeposition (Blanchard et al., 1960; DOE, 1997; Johnston et al., 1991):

Actinium	Cadmium	Gold	Lead	Promethium	Rhenium	Strontium	Tin
Americium*	Cobalt	Hafnium	Neptunium*	Protactinium*	Ruthenium	Tellurium	Uranium*
Antimony	Copper	Indium	Nickel	Radium*	Selenium	Thallium	Yttrium
Bismuth	Curium*	Iron	Plutonium*	Silver	Thorium*	Zinc	

* primarily alpha-counting applications

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, the technique may not be optimal for certain applications. For various reasons, other methods of test-source preparation may be superior. The presence of other metals sometime

interferes, the quality of deposition might be poor (flaking), the recovery can be low, the spectral resolution may 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 alpha spectrometry because of the thickness of the deposit" (DOE, 1997). 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). In addition, ^{54}Mn sources have been successfully prepared by the electrodeposition from mixed-solvent electrolytes onto stainless steel planchets (Sahoo and Kannan, 1997). ASTM D3865 provides a standard test method employing electrodeposition for the isotopes of plutonium.

If the redox couple between the metal cathode and the radionuclide to be deposited is positive, the radionuclide will deposit spontaneously. (One side of the disk may be covered with tape or acrylic spray so that deposition occurs only on the other.) That is, it will deposit quantitatively without using any applied potential. Generally, a metal planchet (disk) simply is 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.

$$Po^{+4} + 2\ Ni \rightleftharpoons Po + 2\ Ni^{+2} \qquad\qquad E^o = 0.98\ volt$$
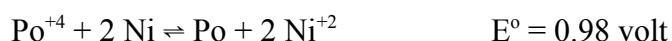
Polonium also will deposit spontaneously on silver planchets. Po-210 is an important naturally occurring radionuclide that is often included in environmental studies. Spontaneous deposition onto nickel, silver, or copper disks is the preferred technique for preparing ^{210}Po sources for measurement.

A similar technique, called internal electrolysis, is preformed by selecting electrodes that have a large difference in potential. No applied voltage is required for these techniques. A conventional electrolytic cell containing an acid solution of the radionuclide to be deposited may be used. A magnesium ($E^o = +2.37$ 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; Van der Eijk et al., 1973).

15.3.2 Precipitation/Coprecipitation

Another attractive technique used to mount sources for alpha spectrometry is microprecipitation. The classical techniques of precipitation utilize milligram to gram quantities of materials in order to make accurate mass measurements. Since such a relatively large mass of material would have a significant impact on sample self absorption and alpha peak shape, the classical method cannot be used. Typically, 0.1 to 1.0 μg of a highly insoluble lanthanide (commonly Nd, Ce, or La) is added to the sample being processed just prior to the final separation of the actinide. This is followed by the addition of hydrofluoric acid to the solution, which causes precipitation of the lanthanide and coprecipitation of the actinide (ASTM D3084 and C1163). A quantitative, micro-pore filter (usually 0.45 μm) is used to separate the precipitate from the supernate. This is necessary because the low mass and concentration of materials forms a precipitate of fine-sized particles. The micro-pore filter allows a slower filtration rate yielding a more uniform deposition of the precipitate in a thin film. Some radiochemists prefer this 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 alpha spectra for uranium, plutonium, americium, and thorium."

Although sources prepared by coprecipitation are generally thicker than those prepared by electrodeposition, sufficiently thin sources, even for alpha spectrometry, can be prepared by controlling the amount of precipitate formed. Actinide sources thinner than 0.5 μg/mm^2 can be prepared by coprecipitation (EPA, 1984a). Thicker sources lead to degraded resolution of the spectra (Hindman, 1983) and sources produced by any technique that are greater than 10 μg/mm^2 lead to attenuation of alpha particles (Adolff and Guiallaumont, 1993). Typical rare-earth carrier masses for microprecipitated sources range between 25 and 100 μg.

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 and is required for efficient source preparation. With suction applied, the precipitate typically is washed with water and then ethyl alcohol (sometimes acetone) to dry the precipitate. The filter is removed from the filtering apparatus and mounted on a metal planchet, commonly with double-stick tape or a glue stick, and stored in a desiccator to await counting. Self adhesive planchets are also used effectively. 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 with radionuclides listed in Table 15.1 have been prepared for quantitative analysis by coprecipitation or precipitation.

TABLE 15.1 — Radionuclides prepared by coprecipitation or precipitation

Radionuclide	Carrier	References
^{32}P*	$MgNH_4PO_4$	a
^{51}Cr*	$BaCrO_4$	a
$^{89/90}$Sr*	$SrCO_3$	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 (1984a)	c	DOE (1997)	e	Sill (1981)
b	EPA (1980)	d	Hindman (1983)	f	Hindman (1986)

* precipitation

It should be emphasized that precipitated sources should 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 test-source loss and contamination of counting equipment. A thin film may also be made by preparing a solution of colloidion and isoamyl acetate. When a 1:1 solution of this mixture is dispersed on distilled water, a thin film is created that can be placed over the source to prevent contamination. Care should be taken to avoid excessive handling of the source that can change the physical nature of the co-precipitate, producing an uneven thickness.

15.3.3 Evaporation

When a high degree of 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 types of measurements. Water samples for gross alpha and beta screening measurements are often prepared by this method (EPA, 1980; EPA, 1984a). 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 50 mm in diameter, and evaporated to dryness under a heat lamp or in an oven. The planchet, with the evaporated test source, may then be 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 may not be flamed if volatile radionuclides (such as Cs, Po, or I) are to be measured.

A commonly encountered problem occurs when 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 precipitating and settling the active material prior to evaporation (Friedlander et al., 1981; 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. 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 requires that the sample aliquant be limited to what will produce 5 mg/cm^2 of solids on the planchet. Thus, for a 50.8 mm planchet (~20 cm^2), an aliquant containing 100 mg of nonvolatile dissolved solids is the maximum test-source mass.

APHA (1998) emphasizes that some low-energy alpha particles (< 8 MeV) will be stopped if covered by only 4 mg/cm^2 of sample solids. For gross beta-particle counting, a solids thickness of 10 mg/cm^2 or less is recommended. Mills et al. (1991) successfully used water sample conductivity to estimate the concentration of dissolved matter in a water sample. The maximum water sample volume that could be evaporated to meet the EPA solids limit of 5 mg/cm^2 can be calculated from this conductivity measurement.

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 may contaminate the detector. Sources consisting of loose, dry material, or with a tendency to flake, may be covered with thin plastic or immobilized by evaporating a few drops of a lucite-acetone solution on the solid deposit (PHS, 1967a).

The use of metal planchets for mounting sources is very common for most alpha, beta and gamma counting techniques. 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, 1967a). Some factors that should be considered in selecting a planchet are:

- CHEMICAL REACTIVITY. The metal planchet should 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 should be measured and corrections applied as necessary for each batch of planchets used.

- SIZE. Two-inch (5 cm) 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 (2.5 cm) planchets are generally used for alpha spectrometry test sources.

- CONFIGURATION. Planchets can be procured in high-walled and low-walled configurations, each with a flat or ribbed bottom. Flat-bottomed planchets are preferred for swipes, air particulate filter samples, and test-source precipitates (or microprecipitates) on filter papers. Ribbed-bottomed planchets, made with a series of raised (ribbed) concentric rings, are typically used for evaporated and chemical precipitate test sources. Precipitates or evaporated residue test sources prepared in a ribbed-bottom planchet that was rotated under a heat lamp tend to be more uniformly distributed compared to sources prepared in a flat-bottomed planchet. The user normally selects a low-walled (3.2 mm wall height) or a high-walled (6.4 mm) planchet depending on the amount of sample to be placed in the planchet and the possibility of the test source creeping up the side of the planchet.

- 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 ensure 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 ensure that they are not contaminated.

15.3.4 Thermal Volatilization/Sublimation

Vacuum thermal volatilization or sublimation is often used when very thin and uniform sources are required (Blanchard et al., 1957; Friedlander et al., 1981). The disadvantages of this technique are that it is time consuming and the recoveries are often less than 50 percent (NAS/NRC 1962).

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 a couple of centimeters 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).

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). 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; Coomber, 1975). 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.

15.3.5 Special Source Matrices

15.3.5.1   Radioactive Gases

Gaseous radionuclides most often measured include tritium, both as a vapor (^{3}HOH) and in the elemental form (^{3}H-H), ^{14}CO$_2$, and the noble gases, ^{37}Ar, ^{41}Ar, ^{85}Kr, ^{222}Rn, ^{131m}Xe, and ^{133}Xe.

Tritiated water vapor often is 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 collected water is analyzed by liquid scintillation spectrometry (EPA, 1984b). Tritiated water vapor is sometimes collected by pulling air through a trap containing materials like silica gel (SC&A, 1994) or through a molecular sieve. 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). For this method, it is very important to de-aerate the liquid prior to introducing the gas, and the temperature should be carefully controlled since gas solubilities are temperature dependent (NCRP, 1978), 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 et al., 1981; NAS/NRC, 1962; Bleuler and Goldsmith, 1952). For example, tritiated water can be reduced to hydrogen gas (^{3}H$_2$) by passing water vapor over a bed of hot zinc, and sodium carbonate can be converted to carbon dioxide (^{14}CO$_2$) with an acid (NCRP, 1978). 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 ensure a 100 percent exchange (EPA, 1984b). 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 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 high-pressure bottles to about 20,800 kPa (~ 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 5 cm (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: (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 28 to 56 L/min (1–2 ft^3/min). 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.

15.3.5.2   Air Filters

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 should 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.

15.3.5.3   Swipes

Swipes (also called "smears") are collected to determine the level of removable surface contamination. They are normally taken on a filter or fabric pad by rubbing it over a predetermined surface area, nominally 100 cm^2. Swipes are routinely counted directly in a proportional counter or liquid scintillation 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 given in the previous section concerning contamination for air filters applies as well 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. When counted in a gas proportional counter, wet swipes should be allowed to air dry prior to counting in order to avoid self-absorption of the alpha and beta particles by the liquid remaining on the swipe (see Section 10.6.1 for further information on swipes). Ensuring that the swipes are dry before counting is important for gross alpha counting measurements. Wet swipes, especially those used to detect removable tritium contamination, normally can be counted using a liquid scintillation without sample preparation. In this instance, it is important that the swipe material be translucent to the radiation emitted by the fluor.

15.4   Alpha Detection Methods

15.4.1 Introduction

When compared to other radioactive particle emissions (such as beta particles), alpha (α) particles are relatively massive. As a result, alpha particles expend their energy over short distances and typically exhibit limited penetration into materials. Alpha particles are also characterized by an intense, high rate of energy loss while passing through matter (see ICRU, 1992, for a discussion of dose equivalents and linear energy transfer). The high rate of energy loss produces dense ionization or intense scintillation which is used to differentiate alpha radioactivity from other types of radiations (beta and photon emissions). Practically, this high rate of loss of energy when passing through matter, requires more stringent sample processing and final sample mounting for alpha counting than is necessary for other types of radioactive counting sources. Examples of direct alpha counting to determine total alpha activity are given in ASTM C799, D1943, and D3084.

Alpha radioactivity normally can be measured by several types of detectors in combination with suitable electronic components. The alpha detection devices most widely used are ionization

chambers, proportional counters, solid-state (silicon) semiconductor detectors/spectrometers, and scintillation counters (plastic, ZnS phosphor-photomultiplier tube combination, or a liquid cocktail). The associated electronic components in all cases include high-voltage power supplies, preamplifiers, amplifiers, pulse discrimination, scalers, and recording devices. For spectrometry systems, an analog-to-digital converter (ADC) and a multichannel analyzer (MCA) would be included in the list of components.

Accurate alpha particle measurements will depend on a number of parameters. The most important of these parameters are:

- Test-source geometry;
- Self absorption;
- Absorption in air and detector window;
- Coincidence losses; and
- Backscatter.

These parameters 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 test and calibration sources. In addition, many of these parameters are discussed in Sections 15.2 and 15.3 on the preparation of sources.

Alpha-particle counters typically have low backgrounds and, in many cases, high efficiencies (10 to 100 percent). Because of their short range (about 20 µm) in common materials, only alpha particles from radionuclides in materials very near the sensitive volume of the detector will be detected. Alpha particles from radionuclides in materials farther away from the sensitive volume of the detector, e.g., detector shields, vacuum chambers, source mounts, structural materials, etc., will not be detected. However, some counters are easily contaminated internally and care should be taken to avoid contamination. These include internal gas flow proportional counters and solid-state detectors. Controls should be put in place that minimize the potential for, and detect the presence of, contamination. Solid-state detectors operated in a vacuum may become contaminated because of recoil from sources (Merritt et al., 1956, Sill and Olson, 1970). Some alpha detectors are sensitive to beta radiation (Blanchard et al., 1960; Hallden and Fisenne, 1963). In these cases, electronic discrimination is often used to eliminate or reduce the effect of the smaller resulting voltage pulses because of beta particles. A discussion of alpha-particle attenuation can be found in Sections 15.2 and 15.3.

Alpha calibration standards are available from NIST or a commercial vendor (complying with ANSI N42.22) that supplies NIST-traceable sources. Among the radionuclides available are ^{230}Th, ^{241}Am, ^{235}U, ^{239}Pu, ^{228}Th, ^{238}U, and ^{226}Ra   (Table 15.2). Other radionuclides are also available. It is critical that calibration sources be prepared in the same precise geometry and manner as the test sources. The calibration 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.

TABLE 15.2 — Nuclides for alpha calibration

Purpose	Nuclide	Reference
Specific Nuclide and Gross Alpha	^{239}Pu, ^{241}Am, ^{210}Po, ^{228}Th, ^{230}Th, ^{226}Ra, ^{233}U, ^{235}U, and U_{nat}	ASTM D3648 40 CFR 141.25(a)
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 (1998), Method 7110

15.4.2 Gas Proportional Counting

The gas proportional (GP) counter is one of the most widely used alpha-particle detection systems. GP counting methods are often referred to as "gross alpha" detection methods because the detector does not differentiate nuclides based on alpha particle energy. GP counters are available in both "windowed" and "internal" (or "windowless") configurations. Both types of GP counters use a special counting gas during operation. Internal GP counters have the detector configured so that there is no window between the test source and the counting chamber. Although windowless GP counters previously have been considered impractical for routine operations, modern windowless counters have been engineered to optimize detector geometry/efficiency while minimizing contamination. Because the efficiency of these systems can be greater compared to the windowed GP detectors, their use should be considered when determining the appropriate system for alpha particle measurements. Windowed GP counters have a thin membrane (Mylar™ or other special materials) window between the test source and the counting chamber. Windowed GP counters are available commercially with window thicknesses between 0.08 and 0.50 mg/cm^2.

There are several types of commercially available GP counters. These include sequential multiple sample (test source) GP counters and multiple detector single sample (test source) GP counters. Each type of counter can be operated to detect alpha and beta emissions, either separately or simultaneously. Normally, between 50 and 100 prepared test sources can be loaded into a sequential multiple sample (test source) GP counter and counted sequentially for a standard counting interval. A multiple detector unit, also referred to as a "shelf" unit, typically has provisions for four detectors per shelf. These multi-detector units can be "networked" together in groups up to 64 counting chambers.

15.4.2.1 Detector Requirements and Characteristics

As an incident alpha particle enters the sensitive volume of the GP detector, primary 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 (volts DC)

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 positive anode. This effect, known as "gas multiplication," is used to amplify (about 1,000 times) the number of gas ions initially produced and the electrical charge (electrons from ionization process) collected at the anode. As with ionization chambers, the charge collected at the anode (through a resistor-capacitor [RC] circuit) results in a change in the voltage potential and the generation of a voltage pulse. As a result of gas multiplication, the voltage pulse produced is considerably larger than the pulse produced in an ionization chamber. When operated at the correct detector high voltage bias, the magnitude of the voltage pulse produced is proportional to the original number of ion pairs formed by the incident particle.

The most common counting gas used in commercial units is a purified 90 percent argon and 10 percent methane gas mixture referred to as " P-10." However, a mixture of 4 percent isobutane and 96 percent methane, and pure methane, also have been used with success. The operating voltage of a detector using pure methane is nearly twice the operating voltage for P-10 gas. Commercial manufacturers of gas proportional counters recommend a P-10 gas purity specification that limits the concentrations of hydrogen, nitrogen, oxygen, carbon monoxide, carbon dioxide, moisture, ethane and methane. Windowed-type detectors may be a sealed type that has a finite amount of the counting gas in the sensitive volume of the detector or a gas flow type wherein the gas flows continuously through the sensitive volume of the detector. Commercial units typically use a gas flow type detector operating with a flow rate of approximately 50 mL per minute.

Gas proportional detectors generally are constructed of stainless steel, oxygen free/high conductivity (OFHC) copper, or aluminum. Commercial GP counters have detectors with diameters between 25.4 mm and 133 mm. Most commercially available automated GP counters have a detector size of 57.2 mm (2.25 inches). Test-source mounts, normally stainless steel planchets, accommodate test sources of similar diameters and heights up to 9 mm. The manufacturer's specifications for a GP counter of either type should include performance estimates of a background count rate, length and slope of the voltage plateau, and efficiency of counting a specified electrodeposited calibration source, along with the type of gas used in the tests. For a windowed GP counter, the window thickness is important and the user may want to compromise on the thickness for both alpha and beta counting applications. A thin window is needed for counting nuclides having alpha and low-energy beta emissions. Common window thicknesses offered by the manufacturers include 0.08 and 0.50 milligrams per square centimeter. For GP alpha-particle counting, typical values for the important operational parameters are provided in Table 15.3.

One instrument manufacturer has engineered a windowless GP counter available as a sequential multiple sample (test source) or a multiple detector single sample (test source) GP counter. The units available typically have lower alpha background and higher detector efficiency specifications compared to windowed GP counters.

TABLE 15.3 — **Typical gas operational parameters for gas proportional alpha counting**

Background count rate (57 mm diameter detector)	3–10 counts/hour or 0.83 to 2.8×10^{-3} cps
Length of voltage plateau	300–800 V DC using P-10 gas
Slope of voltage plateau for well-designed detector	1–2.5%/100 V for an electroplated source
Windowless detector efficiency $- \dfrac{100 \times \text{count rate}}{\alpha \text{ emission rate}}$	49–51% for an electroplated source including backscatter
Windowed efficiency $(0.8 - 0.5 \, \text{mg/cm}^2 \text{ thickness}) - \dfrac{100 \times \text{count rate}}{\alpha \text{ emission rate}}$	30–40% for an electroplated source

SHIELDING

The purpose of shielding is to reduce the background count rate of a measurement system. Shielding reduces the background count rate by absorbing some of the components of cosmic radiation and radiations emitted from materials in the surroundings of the measurement system. Ideally, the material used for shielding should itself be free of any radioactive material that might contribute to the background. In practice, this is difficult to achieve as most construction materials contain at least some naturally radioactive species (such as ^{40}K, members of the uranium and thorium series, etc.). However, most alpha detectors are quite insensitive to the electromagnetic components of cosmic and other environmental radiations. In addition, when properly operated, the alpha particle detector or detection system will be insensitive to, or will electronically discriminate against, beta particles. Because of their short range, alpha particles from outside sources will not penetrate the active area of the alpha detector. Therefore, a minimum amount of shielding is necessary for alpha particle GP counting of test sources. However, most low-background GP systems are used for beta-particle measurements as well and, as such, shielding is needed to reduce the beta background count rate.

BACKGROUND

Most of the commercial GP counting systems have passive detector shielding and active cosmic guard (anti-coincidence counting detectors/circuits) systems to reduce a detector's background. However, these background reduction methods are more applicable to beta-particle measure-ments than to alpha-particle measurements. This is because the short range of alpha particles in common materials (about 20 μm) allows only alpha particles from radionuclides in materials near the sensitive volume of the detector to be detected. To reduce the alpha (and beta) background, the detector manufacturers purposely construct detectors from materials that have a minimum amount of naturally occurring radioactivity, e.g., trace amounts of uranium and thorium.

The alpha particle background for gas proportional counters will depend upon detector size. For

some commercial units with a 57.2 mm diameter detector with a 0.08 mg/cm² window thickness using P-10 gas, the alpha background count rate is typically under 6 counts per hour (0.1 counts per minute [cpm]). Alpha background count rates of 3 counts per hour (0.05 cpm) may be obtained for commercial GP counters with different detector specifications.

OPERATING VOLTAGE

The operating voltage of a gas proportional counter used in the alpha-particle counting mode depends on the counting gas used, the amplifier and voltage discriminator settings and the mode of alpha particle discrimination—voltage pulse height discrimination or simultaneous alpha and beta particle counting. The configuration of the ionization collection wires within the detector chamber also affects the operating voltage. However, most commercial manufacturers have standardized on a particular configuration. Currently, the most common counting gas used in commercial windowed type GP units is P-10.

Prior to the operation of a gas proportional counter, the operating voltage of the detector must be determined in conjunction with the other operating parameters. Normally, the manufacturer of the unit recommends the voltage discriminator and amplifier gains settings. The user typically places an electroplated alpha source into the counting position and increases the detector bias voltage in discrete 25 or 50 V DC increments while recording the observed source count rate at each voltage setting. Figure 15.1 illustrates a typical voltage response curve for a commercial windowed type gas proportional counter detector using P-10 counting gas and a massless ^{210}Po source (Canberra, 2002). Notice that the count rate levels off after about 500 V DC to form a plateau that extends to about 900 V DC. For most commercial GP units, the slope of this plateau should be 2.5 percent (or less) per 100 volts. For Figure 15.1, the detector operating voltage for alpha counting would be approximately 550 to 600 V DC. Note that on the beta (beta plus alpha) plateau region of approximately 1200 V_{DC}, there is a 35 percent increase in the ^{210}Po count rate. When using the separate alpha plateau then beta (plus alpha) plateau-counting modes, the increase in the alpha-particle count rate on the beta plateau must be determined at the alpha and beta plateau voltages selected during calibration (i.e., determining the ratio of the alpha-particle count rate on the beta plateau to the alpha-particle count rate on the alpha plateau). For test-source measurements, the observed beta-particle count rate must be adjusted for the alpha-particle count rate on the beta plateau by applying a correction factor using this ratio. The observed increase in the alpha count rate on the beta plateau varies
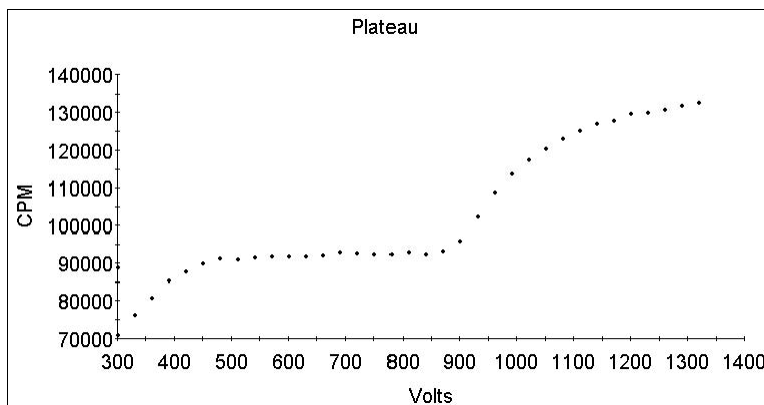
FIGURE 15.1 — Alpha plateau generated by a ^{210}Po source on a GP counter using P-10 gas

according to the alpha emitting nuclide. The difference between the count rates on the two plateaus will be accentuated for nuclides that have both alpha and photon emissions, e.g., ^{241}Am.

For the simultaneous alpha and beta counting mode, the detector operating voltage is located on the beta-particle plateau (Section 15.5.2.1). For this counting mode, the voltage discriminator setting for alpha detection is set so that only a small fraction (less than 1 percent) of the beta detection events will be registered as alpha detection events.

CROSSTALK — REGISTRATION OF BETA PULSES AS ALPHA PULSES

Modern proportional counters are capable of differentiating between alpha and beta interactions in the detector. This is accomplished by identifying the two types of particles based on the resultant voltage pulse heights from their interactive events in the detector. As discussed previously, the interaction of an alpha particle with the counting gas generates substantially more primary ionization events and, thus, a higher resultant voltage pulse compared to a beta particle. Those voltage pulses whose heights exceed an experimentally established alpha voltage discriminator level are registered as alpha counts and those falling below this level are recorded as beta counts. The dynamic range of the voltage separation between the alpha and beta voltage pulses varies by detector design and manufacturer. For some GP counters, depending on the beta particle energy and voltage (pulse) discriminator setting, some small fraction—usually less than 1 percent for a ^{90}Sr/Y ($E_{\beta max}$ = 2.28 MeV) massless point source counted in the simultaneous counting mode—of the detected beta particles may be recorded as alpha particles. This misclassification of alpha and beta measurement events (counts) is referred to as "crosstalk" or "spillover." The degree of spillover varies according to detector design and GP counter manufacturer.

For some commercial GP counters, crosstalk may occur for both modes of GP counting, i.e., alpha then beta plateau counting and simultaneous alpha and beta counting. For electroplated beta particle sources, the crosstalk is minimum for both counting modes when the voltage (pulse) discriminator is properly set. The beta-to-alpha crosstalk should be evaluated for all applications (i.e., test sources that are massless and not massless).

For both types of counting modes (plateau counting or simultaneous alpha/beta counting), corrections should be made to the alpha-particle count rate to remove the portion contributed by beta particles when significant beta activity is present (greater than 1 percent of the alpha activity). Since the fraction of the beta counts occurring in the alpha channel depends on the beta particle energy and source mass, a crosstalk curve should be developed. The same beta emitting radionuclide selected for the beta particle self-absorption curve should be used for the crosstalk determination. The crosstalk curve would relate the fraction of beta particles counted as alpha particles as a function of source mass. A crosstalk response curve is generated by recording the alpha counts from the beta self-absorption determination at all source masses and plotting the crosstalk fraction (beta count rate in the alpha channel/beta count rate beta channel) as a function of source mass (Section16.4, "Data Reduction on Non-Spectrometry Systems"). Alpha count

rates then can be corrected for the influence of the beta particles at all source thicknesses.

15.4.2.2   Calibration and Test Source Preparation

Calibration and test sources for proportional counters are usually prepared by electrodeposition, coprecipitation, or evaporation, as described in Section 15.3. For internal counters, since the source is placed within the detector, care should be exercised in source preparation to avoid the inclusion of chemicals that may react with the detector materials. Likewise, any spillage of source material can result in contamination of the detector.

The absorption of alpha particles in the source material (self-absorption) should 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, 1985). Thus, to approach absolute counting in either 2π or 4π counting geometries, test sources should be prepared as thinly and uniformly as possible. Electrodeposited sources provide the most uniform sources for evaluating these parameters.

Another method sometimes used for alpha-emitting test sources in ionization and GP counters is to perform the count at infinite thickness (Sections 15.2 and 15.3). The count rate of a test source at infinite thickness usually is related to the count rate of a calibration source prepared and measured in the exactly the same manner. However, this application is best used when the calibration is for a well known single nuclide source or a source term wherein the multiple nuclide concentration ratios do not vary substantially. The method is less accurate when applied to a mixture of nuclides having different alpha energies and varying concentrations.

Backscatter from alpha sources increases with the atomic number of the backing or source material and with decreasing alpha energy (NAS/NRC, 1962). 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). When stainless-steel planchets are used, the increase in a count rate because of alpha backscatter is only about 2 percent (PHS, 1967a).

15.4.2.3   Detector Calibration

Gas proportional counters should be calibrated according to their intended use (i.e., nuclide specific or gross alpha measurement applications). Gross alpha measurements, as the name implies, are nonspecific to a given alpha-emitting nuclide or the isotopes of an element (uranium or radium) and typically require no chemical separations or purification steps. The most common applications for gross alpha measures are health physics swipes for contamination surveys, air particulate filter papers from air monitoring programs and evaporated surface or ground waters onto a metal planchet. For gross alpha measurements, the instrument's calibration is related to a reference nuclide, typically one that is specified by a laboratory client, measurement quality

objectives or by regulatory requirements. Typical alpha-emitting reference nuclides include ^{241}Am, ^{237}Np, ^{210}Po, ^{239}Pu, ^{228}Th, ^{230}Th, and U$_{nat}$.

Calibrations for alpha particle measurements can be accomplished for either the alpha plateau counting mode or the simultaneous alpha and beta counting mode. However, for both modes of operation, calibration sources should be prepared in a manner identical to the method used for test-source mounting. This may include massless or electroplated sources, microprecipitated (< 200 µg) sources and low mass (1–125 mg) sources. For accurate results for both counting modes, alpha-particle self-absorption curves and crosstalk corrections should be developed during calibration of the GP counter.

Calibration sources prepared for calibrating counters for a specific nuclide measurement should contain a radionuclide of similar alpha energy and be measured under identical conditions as the test sources to be measured (ASTM D3648). Alpha calibration standards are available from a national standards body such as NIST or as NIST-traceable sources from a commercial vendor that complies with ANSI N42.22. 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. See Table 15.2 (Section 15.4.1) for a list of available for alpha-emitting nuclide calibration sources.

The counting efficiency (ε) is determined by counting a calibration source to accumulate sufficient net counts (approximately 10,000) to provide a relative (1σ) counting uncertainty of about 1 percent and dividing the resultant net count rate (cps) by the alpha emission rate of the source (α/s). The alpha emission rate is determined by the source activity (Bq) times the alpha abundance per disintegration:

$$\varepsilon = \frac{\text{Measured Net Count Rate (cps)}}{\text{Bq} \times \text{fractional } \alpha \text{ abundance}}$$

For a nuclide-specific or reference-nuclide counting efficiency, the same equation is used but without the alpha abundance factor. The uncertainty of the detector efficiency factor can be calculated using the methods described in Chapter 19 (*Measurement Uncertainty*).

For health physics swipes and air particulate filter samples (test sources), a calibration source is prepared by spiking an unused filter with the appropriate calibration solution. For health physics swipes, the entire surface of the filter paper may be spiked. However, only the active area of an air filter paper is spiked with the calibration solution. The retainer ring and gasket holding down the filter determines the active area to be spiked. Depending on the filter composition (e.g., glass fiber filter), the filter matrix may cause some wicking of the solution away from the surface. In order to prevent the wicking effect, the surface of the filter may be sprayed with an acrylic lacquer and dried prior to spiking the surface.

Attenuation or self-absorption corrections may be necessary for alpha counting. Attenuation corrections should be made whenever the test-source matrix differs from that of the calibration source. 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 generally will be necessary with a test-source density thickness greater than about 1 mg/cm^2.

In cases where finite test-source thicknesses are unavoidable, alpha-source measurements can be adjusted to account for self-absorption (PHS, 1967a). In order to determine the change in counting efficiency as a function of source thickness or mass, a self-absorption curve must be developed. Calibration sources containing a known amount of the radionuclide of interest are prepared in varying thicknesses (masses) 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 a known amount (sometimes constant) of 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 μg/cm^2 or mg/cm^2 (NCRP, 1978). 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 calibration 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 μg/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 radioanalytical laboratories use a more simplified method to generate a self-absorption curve. A self-absorption curve typically is generated by determining the counting efficiency as a function of source mass in milligrams or mg/cm^2 without normalization to the "zero thickness" efficiency. Figure 15.2 illustrates a typical self-absorption curve for ^{230}Th in a dry residue generated from evaporated tap water.

15.4.2.4   Troubleshooting

Various problems may arise when counting calibration or test sources on a GP counter. These may include instrumentation or test-source preparation related issues. Instrumentation related problems should be identified through the instrument's operational quality control checks that include periodic detector response and background measurements. Section 18.5.6 ("Summary Guidance on Instrument Calibration, Background, and Quality Control") within Chapter18 provides the recommended frequencies for these types of quality control (QC) measurements for a GP counter. Instrumentation problems may arise from electronic component failure or changes, a low flow rate of counting gas delivered to the detector, impure or wrong gas mixture,

The plot shows Fractional Detection Efficiency (y-axis, from 0.10 to 0.50) versus Precipitate Weight (mg) (x-axis, from 0 to 60+).

Fitted equation: $y = 0.453 - 0.0417\ x^{0.5}$

95% confidence limits
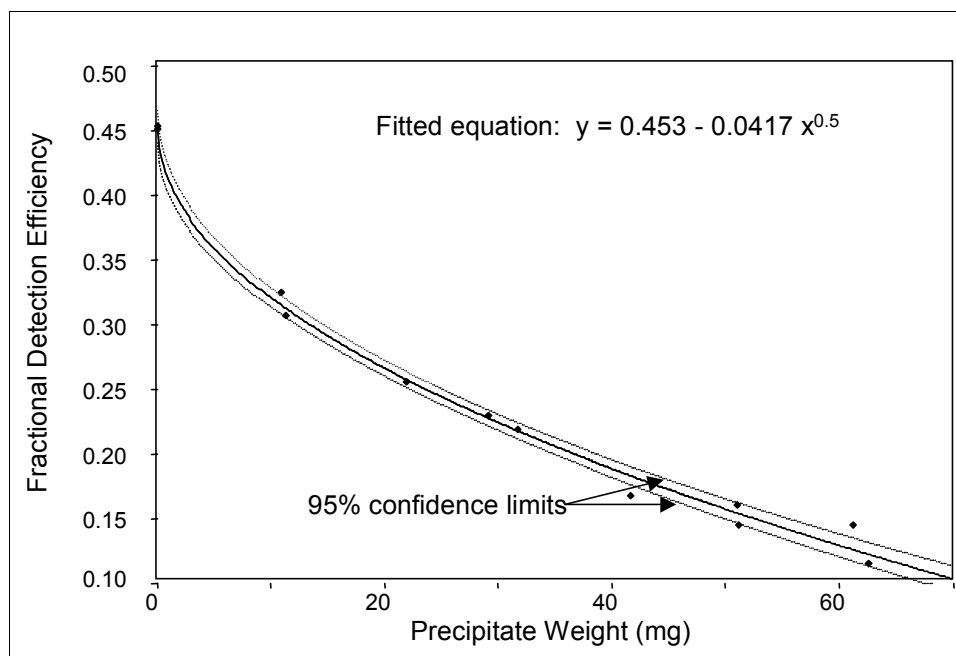
FIGURE 15.2 — Gas proportional counter self-absorption curve for ^{230}Th

malfunction of guard ring, harsh operating environment such excessive temperature and humidity, poor electrical power with excessive noise or radio frequency interference and grounding effects. Identification of an intermittent problem, such as electrical noise, is generally more difficult than identifying a consistent problem such as an instrument component failure. Detector contamination from highly radioactive samples or loose material on a test source (air particulate filters or swipes) may lead to inaccurate results if an increased detector background is not quantified and subtracted from subsequent test-source measurements.

Inaccurate results can occur from the misuse of a specific nuclide detector calibration or if the test sources are prepared differently than the calibration sources. For example, using an alpha self-absorption curve based on a nuclide(s) having a low-energy alpha(s) (e.g., natural uranium) to calculate the activity in test sources containing nuclides of higher alpha energies (e.g., ^{226}Ra plus progeny) may produce inaccurate results. It is important that a laboratory and its client decide cooperatively on the reference nuclide for gross alpha measurements as well as the chemical composition of the calibration sources to generate the self-absorption curve. Some clients may want the laboratory to use the gross alpha reference nuclide that the nationally recognized performance evaluation programs incorporate into their gross alpha test samples.

Inaccurate results also may occur when an alpha detector efficiency factor for a massless calibration source is applied to air particulate and swipe test sources. The magnitude of the inaccuracy depends on many factors affecting alpha self absorption, including the depth of filter penetration by particles, which is a function of flow rate and the type of filter material (e.g., membrane, glass fiber, Teflon®, cotton), and dust or material loading. Dust loading of air filters is

a function of the airborne dust concentration, air flow, and sampling duration. For most environmental surveillance programs monitoring airborne contaminants, the air flow and sampling duration are limited to prevent significant and undesired dust loading. When there is minimal dust loading on a filter, such as from short-duration sampling at relatively low flow rates, only a small reduction in the counting efficiency because of alpha self-absorption may be observed. Loysen (1969) indicated alpha self-absorption losses to be about 6 percent for glass and membrane (5 μm pose size) filters used to collect radon progeny, typically in a 20 L sample collected over a 10-minute interval. McFarland (1998) found that air filter and swipe sample results could be "under reported" by applying a detector efficiency factor for electroplated sources to these sample matrices. In the study, the GP detector efficiency for an electroplated [241]Am source was 0.485, while the detector efficiency for clean and slightly dirty (5-6 mg) swipe samples was 0.292 and 0.243, respectively. For Mylar®-covered simulated air filters, detector efficiencies of 0.229 and 0.199 were observed for Mylar coatings of 0.5 and 0.85 mg/cm^2, respectively. A discussion and recommendations on the analysis of health physics smear samples by GP counting can be found in ANSI N25.25, Annex B.5.

15.4.3 Solid-State Detectors

Semiconductor detectors used for charged particle spectrometric applications provide many advantages compared with the other alpha detectors. These include good energy resolution, stability or minimal drift in energy response, excellent signal timing characteristics, very thin entrance window to minimize particle energy losses, and simplicity of operation (Knoll, 1979). Solid-state or 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.

There are three technologies used by manufacturers for the production of solid-state alpha detectors made of silicon: diffused junction, surface barrier, and ion-implanted. The detectors can be made partially depleted or totally depleted. These detectors are mostly made of n-type base material. Currently, the majority of semiconductor detectors in use for alpha spectrometric applications are the ion-implanted detector. The semiconductor material must have a high enough resistivity to give the required depletion depth. The depletion depth is the sensitive depth of a detector where charged particles interact with the semiconductor material particle to produce electron-hole pairs and must be thick enough to absorb all of the energy of an alpha particle. The interaction of photons with this thin depletion layer is normally negligible. Since the detector shows a linear response with particle energy, any interactions of beta particles with the detector can be eliminated by electronic discrimination.

When a reverse bias voltage is applied to a semiconductor detector, a leakage current is generated. The leakage current of silicon diodes doubles for every 5.5–7.5 °C rise in ambient temperature. Because the preamplifier high voltage bias resistor adds noise, it is necessarily of

high value, typically 100 megaohm. Since a surface barrier detector can have a leakage current in the tenths of microampere, the voltage drop across the bias resistor can be substantial. A couple of degrees rise in the temperature will significantly increase this voltage drop, thereby reducing the voltage at the detector. This bias change can be enough to affect the overall gain of the detector-preamplifier by a substantial amount. The ion-implanted detector, on the other hand, has leakage currents in the nanoampere range and thus does not produce a substantial voltage drop across the bias resistor. The system is therefore not as strongly dependent on temperature.

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 3.6 eV and in germanium is 2.96 eV (Gilmore and Hemingway, 1995) 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. In addition, the rise time of a voltage pulse is very fast (~10 ns) and the voltage pulse height does not vary with count rate. (Mann et al., 1991)

15.4.3.1   Detector Requirements and Characteristics

An alpha-particle spectrometry system typically consists of a solid-state detector in a vacuum chamber, high voltage detector bias supply, charge-sensitive preamplifier, amplifier, ADC, and a digital memory storage device. In older systems, the ADC and the digital memory storage device were combined into a multichannel analyzer unit. More recent systems use a computer for the memory storage device. In some multiple detector spectrometry units, the ADC contains a multiplexer to acquire each detector's spectrum and to control the operational aspects of each detector. Alpha-spectrometry systems normally are operated to cover the energy range between 3 and 8 MeV for most long-lived nuclides. However, typical systems can be operated from 0 to 10 MeV. For example, the upper energy range can be extended to 10 MeV for quantifying short-lived nuclides such as ^{212}Po and ^{214}Po. An alpha spectrometry system's gain can be selected according to the application and system components but a gain of about 10 keV per channel is common. There are several commercial manufacturers of alpha spectrometry systems, alpha detectors and electronic components.

Four parameters normally are specified when selecting a detector for charged-particle spectro-metry. These include resolution, active area, depletion depth, and background. Commercial manufacturers (ORTEC, 2002; Canberra, 2002) have produced a selection of detectors that vary in these four parameters. For most alpha spectrometric applications, a depletion depth in silicon of approximately 100 μm is sufficient. If the detector is used for other charged particle applica-tions (beta or proton), detectors having a depletion depth of 500 μm and greater are available. For alpha particle spectrometry applications, the resolution of a detector increases in a nonlinear fashion as the active detector area increases. Although commercially available detectors are available with an active area between 25 and 3,000 mm^2, a typical alpha-spectrometry detector has a 450 mm^2 active area.

The full-width-half-maximum (FWHM) resolution of an alpha spectrometry system using commercially available detectors depends on several parameters that include; inherent energy resolution of the detector, charge carrier statistics, incomplete charge collection and variations in the energy loss in the dead layer, i.e., entry window thickness. The noise contributions from the nondetector system components to the energy spectrum is minimal for most alpha spectrometry systems.

The quoted resolution specification by a manufacturer is based on an ultra-thin source measured in a vacuum at a source-to-detector distance of 1.5 times the detector's active diameter. Typical detector resolutions, as measured for the 5,486 keV alpha line of ^{241}Am, vary from 15–50 keV for detector areas between 50–2,000 mm^2. For a nominal detector size of 450 mm^2 with a 100 μm depletion depth, a typical detector resolution is about18 to 20 keV. Manufacturers have also produced "ruggedized" ion-implanted contact detectors whose detector surface characteristics permit cleaning in case of contamination. The resolution of these ruggedized detectors is similar to the other detector types or about 20 keV. Some general characteristics and requirements for the detector operation are described below.

OPERATING VOLTAGE

Silicon semiconductor alpha detectors operate at a low reverse bias voltage condition, normally between 50–100 volts DC. The voltage bias supply should be highly regulated to prevent noise and loss of resolution. The polarity of the bias depends on the type of detector, e.g., surface barrier, etc. To avoid possible damage, a voltage bias should not be applied to the detector while exposed to light. Many commercially available multiple detector units have an interlock system for each vacuum chamber that removes the detector bias if the chamber is opened to the atmosphere.

BACKGROUND AND SHIELDING CONSIDERATIONS

Because of their insensitivity to beta and photon radiations, semiconductor alpha detectors with thin depletion depths are not shielded against external background radiations. The depletion depth of an alpha detector is too thin to develop significant pulses from the interactions from cosmic or gamma rays. Without a shielding requirement, multiple alpha detectors can be mounted in close proximity. Multiple detector units typically have eight detectors, each enclosed in separate vacuum chambers

Following manufacture, the background of an alpha semiconductor detector is nearly negligible. Several factors contribute to the low background characteristic. First, the inherent naturally occurring radioactivity in the ultra-pure semiconductor silicon material of the detector is extremely low. Since the surface area of the detector is small and the contact electrodes are extremely thin, there is only a small amount of material that is available to contribute to the detector background. However, only alpha particles from radionuclides in materials near the

sensitive volume of the detector will be detected. The detector manufacturers purposely construct detectors from materials that have a minimum amount of naturally occurring radioactivity, such as trace amounts of uranium and thorium. A nominal background specification (ORTEC, 2002) for energies above 3 MeV is less than 1.2 counts per day per cm^2 of active detector area, or less than 24 counts per day for a 450 mm^2 surface area detector. Typical observed backgrounds may range from 8–13 counts per day for an energy window between 3–8.2 MeV. Burnett (1994) has reported a typical background for new Planar Implanted Passivated Silicon (PIPS) detectors of the order of 6 counts per day (0.004 cpm) for a 3 to 8 MeV energy region and about 1 count per day (0.001 cpm) under individual regions of interest of about 300 keV.

VACUUM

In order to obtain the best alpha peak resolution, a solid-state detector is operated in a near vacuum condition to eliminate the alpha-particle energy degradation from interactions with air molecules prior to striking the detector face. In addition, surface barrier detectors are operated (with bias voltage applied) in a near vacuum to prevent damage of the surface layer. (Mann et al., 1991) There are several different vacuum chamber designs manufactured for alpha spectrometry applications. However, all units are light tight and have some type of gasket seal to prevent vacuum degradation. Because of the very thin entry window, the detector is very light sensitive and the bias voltage should not be applied when the detector is exposed to light. (Knoll, 1979). Older single detector chamber units were essentially large stainless steel vacuum bells with provisions for the high voltage bias and signal connectors. More recent vacuum chambers are of a smaller configuration and have several shelves to position the test-source mount at different distances from the detector face. Many commercially available multiple detector units have an interlock system for each vacuum chamber that removes the detector bias if the chamber is opened to the atmosphere.

Traditional silicon surface barrier (SSB) alpha detectors typically are operated under a near vacuum that is less than 500 µm Hg. These systems have bias voltage "cut- outs" to protect the detector if the pressure exceeds this value. The balance of air pressure to protect the detector from recoil contamination and loss of spectral resolution limits the range of pressures under which these detector systems have worked. Vacuum pumps are available to permit detector chambers to reach less than 6.7 Pa (50 µm Hg) and, by continuously running the pump, maintain that level indefinitely. In some vacuum systems, an electronic air pressure sensing device is used to monitor the internal pressure in a chamber and to control the operation of the vacuum pump. The PIPS style alpha detectors can be operated at pressures from 1 to 20,000 µm. Higher pressures prevent recoil contamination. Where recoil is not a concern, the operator can lower pressure to achieve the desired spectral resolution. Burnett (1994) has provided detailed information on the optimum air pressure needed to maintain good spectral resolution and to maintain low detector backgrounds for alpha spectrometry systems.

15.4.3.2   Calibration- and Test-Source Preparation

For best results, the calibration and test sources should be isotopically pure and nearly massless. Some radiochemists prefer test sources that have been electroplated to make a lower mass (Puphal and Olson, 1972), while others prefer preparing test sources using a microprecipitation technique. Microprecipitation as fluorides has been reported with only slight loss of resolution (Sill and Williams, 1981; Hindman, 1983).

Alpha-energy spectra of very high resolution are attainable with semiconductor detectors if the prepared test source is essentially massless, ≤ 1 µg/mm^2 (Herpers, 1986). As the thickness of the test source increases, the spectral energy is degraded because of self-absorption, which broadens the peak and forms a tail on the lower-energy side (Section 16.3.2, "Alpha Spectrometry"). 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 (microgram) quantities of precipitate are recovered. ASTM D3865 provides a standard method for the electrodeposition of the plutonium isotopes with subsequent counting by semiconductor detectors. For example, in the coprecipitation of actinide test sources for spectral analysis, source thicknesses of 0.4–1 µg/mm^2 (0.04–0.1 mg/cm^2) are achieved routinely, which is quite adequate for producing well-defined alpha spectral peaks (EPA, 1984a). From a practical point-of-view, FWHM resolutions of 53 keV can be achieved with microprecipitates of about100 µg (0.20 µg/mm^2) for nuclides having well-defined and separated alpha peaks. Sill and Williams (1981) have prepared actinides, with the exception of uranium, on a 25 mm membrane filter (0.1µm porosity) with 50 µg of a strongly alkaline solution of EDTA. Resolutions near 70 keV were typical for this microprecitate mass.

15.4.3.3   Detector Calibration

Calibration sources may be prepared by either electrodeposition or coprecipitation. These sources can be prepared by the laboratory or purchased from commercial sources. Because of their durability and stability, electrodeposited calibration sources are often chosen. However, more recent radioanlytical methods are preparing calibration and test sources using coprecipitation that involves microgram quantities of $BaSO_4$, NdF_3, CeF_3, etc. Refer to Chapter 14 for electrodeposition and coprecipitation methods. 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 additional discussion on alpha spectrometer calibrations in Section 16.3.2.

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 should be known with a high degree of certainty. In selecting an appropriate mixture of radionuclides, one should consider energy range, peak overlap, unresolved secondary alpha peaks, alpha emission abundance, ingrowth of decay progeny, useful life of the source (decay), potential for detector contamination ([210]Po volatility), nuclide availability, and practicality of preparing the multi-nuclide source.

Calibration or QC sources having volatile radionuclides or extremely high activities should be avoided or their use minimized to prevent contamination.

15.4.3.4   Troubleshooting

A number of factors can influence alpha spectrometry results or cause a detector to malfunction. These include a poor detector chamber vacuum, attenuation or self absorption, detector con-tamination, and other radionuclide interferences. Attenuation or self-absorption corrections need not be made if constant massless test sources are used for test and calibration source counting. If constant mass cannot be maintained, then spectral degradation adjustments (increase or decrease region-of interest window size) and/or corrections (subtraction of counts from interfering peak) may have to be made in order to produce accurate results. When there is a single peak, or when peaks are well-separated, the region-of interest window size may be increased in order to integrate the entire peak. When peaks begin to overlap because of the degradation in resolution, the region-of interest window for the upper energy peak may be decreased, but the detector efficiency factor must be adjusted accordingly. The spectral interference in the lower energy peak from the widened upper peak must be estimated and removed. These actions generally will increase the relative uncertainty of the analysis.

Some commercially available alpha spectrometry systems have detailed troubleshooting protocols that cover resolution and vacuum leakage problems based on monitoring the leakage current and vacuum during operation. A resolution problem generated by excessive electronic noise can be evaluated by comparing a newly acquired resolution of a pulser peak to the manufacturer's detector specification. A sudden increase in the leakage current of a detector also indicates a problem. An increase in the air pressure in the detector chamber from a defective gasket seal may be sufficient to degrade a spectrum.

Microprecipitation of CeF_3 and NdF_3 require the precipitation in an excess of hydrofluoric acid (HF). In order to prevent damage to a solid-state detector, it is important that all traces of HF be neutralized or removed from the test source before the test source is inserted into the alpha

detector chamber. Removal of residual HF involves multiple washes of the microprecipitate after filtration. In addition, a NH_4OH chamber has been used to neutralize residual HF on test sources. If left unchecked, the HF damage is typically progressive over time.

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 is recommended by the detector manufacturers and can be provided easily in most environments. 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 checked periodically. Contaminated detectors will have higher background counts. Even when test-source spectra are corrected for the presence of contamination, the higher background results in higher minimum detectable amounts (MDAs). The next section covers detector contamination in detail.

15.4.3.5   Detector or Detector Chamber Contamination

Detector contamination can be a problem, so detector backgrounds should be checked after receipt of the detector from the manufacturer and periodically thereafter (see Section 18.5.6, "Summary Guidance on Instrument Calibration, Background, and Quality Control). Detector contamination may occur quickly or may be a gradual process related to the number of sources analyzed. Even when source spectra are corrected for the presence of contamination, the higher peak background results in a higher minimum detectable activity.

After manufacture, the background for semiconductor alpha detectors is very low, typically ranging from 8 to 17 counts per day (1×10^{-4} to 2×10^{-4} cps) over a 3 to 8 MeV energy range. The detector background may increase after use because of contamination principally from two mechanisms: atom recoil or volatilization of atoms on the test or calibration sources counted in a near vacuum. Recoil contamination takes place when fragments from the test or calibration source travels 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 nondestructively. The recoil fragment of the primary alpha-emitting nuclide may be a single decay product or a string of progeny decay products. 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 progenies are produced. However, if the half-lives in question are very short (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 test sources 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 beta-emitting nuclides ejected by alpha recoil can contribute to alpha background if they subsequently decay to alpha emitters. For example, the direct progeny of ^{229}Th is ^{225}Ra which decays by beta emission to the alpha producing progeny ^{225}Ac.

The degree and rate of contamination from recoil atoms will vary according to the activity of the source, source-to-detector distance and the frequency of source measurement. The closer the source is to the detector, the more likely contamination will occur. It is strongly recommended that energy and efficiency calibration sources have nuclides that are different from the nuclides measured in the test sources. If this is unavoidable, limit the frequency of usage and the counting time to reduce detector contamination from the calibration sources.

Sill and Olson (1970) minimized the contamination caused by recoil by operating a chamber at a lower pressure equivalent to a 12 $\mu g/cm^2$ absorber between the test source and detector and applying a low differential voltage (6 V DC) between the test-source mount and the detector. The authors reported a 1,000-fold reduction in contamination with only a decrease in resolution of 1–2 keV. Burnett (1994) has provided detailed information on maintaining low detector backgrounds for alpha spectrometry systems, including the optimum air pressure needed to maintain a 12 or 16 $\mu g/cm^2$ absorber for various source-to-detector distances. Manufacturers have incorporated these concepts into commercially available detector chamber systems.

Contamination of detectors by polonium isotopes, such as ^{210}Po ($t_{1/2} \approx 138.4$ d), may 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 mechanism, it is clear that polonium activity is indeed transferred to detectors. Detector contamination by volatilization is a very serious problem with long-lived ^{210}Po and even worse when working with ^{209}Po ($t_{1/2} \approx 102$ y) as a yield tracer. In order to reduce detector contamination, calibration or QC sources having volatile radionuclides should be avoided or their use minimized when possible.

Manufacturers warn that nonruggedized surface-barrier detectors cannot be cleaned to remove contamination. However, manufacturers have produced certain types of detectors that may be decontaminated. These include the ruggedized detectors and detectors that have ion-implanted contact immediately under the silicon surface. Swabbing the surface with a cotton swab wetted with a chemical cleaning agent followed by blow drying with clean nitrogen gas is the recommended cleaning process for these detectors. A detector chamber may be cleaned by the same process.

15.4.3.6   Degraded Spectrum

A spectrum is considered degraded when the peak resolution has deteriorated from the ideal or desired resolution to the extent that nuclide qualification or quantification difficulties arise. For most analytical methods, a peak resolution of 20 to 70 keV is attainable for electrodeposited sources and microprecipitated mounts. A degraded spectrum may be related to several causes that include: a detector or electronic component problem, accumulation of dirt or film on the detector surface, a poor or degraded calibration- or test-source mount, an excess amount of material on the test or calibration source or a degraded vacuum from a detector chamber leak.

Electronic noise in a spectrometry system, depending on its severity, may lead to poorer resolution and a broadening of alpha peaks. The noisy component (preamplifier, amplifier, bias supply, etc.) of a system may be identified using a pulser, an oscilloscope, or a component replacement process. Detector manufacturers recommend the identification of a noise generated resolution problem by comparing a newly acquired resolution of a pulser peak to the manufacturer's detector specification.

Contamination of a detector surface from dirt or oils from the hand, etc., can lead to the degradation of a spectrum. The severity of the degradation will depend on the extent of the areal contamination and depth of the material.

An air leak from a defective detector chamber gasket seal can increase the detector air pressure sufficiently to degrade a spectrum. However, the air pressure in the chamber usually has to exceed 1 mm Hg before spectral degradation occurs.

Probably the most prevalent cause of a degraded spectrum is from an undesired excess of material that has been electroplated or microprecitated on a calibration- or test-source mount. As the thickness of the test source increases, the alpha spectral energy is degraded because of a self-absorption, which broadens the peak and forms a tail on the lower-energy side. This broadening results in poor resolution and difficulties in resolving peaks in a spectrum. The resolution needed for a given analysis depends on the number and closeness of the alpha peaks expected in the spectrum. In most cases, multiple alpha emitting isotopes or nuclides are electroplated or coprecipitated on the same counting mount. For these cases, a better resolution is needed compared to a simple one peak spectrum. For most microprecipitate/coprecipitate mounting methods, a final mass less than 130 µg is typical. An additional 60–100 µg of material on a mount can degrade an alpha spectrum to the point where peak interference corrections may be necessary depending on the closeness of the peaks. Most laboratories will develop test-source spectrum resolution cutoff values above which a test-source mount will be reprocessed or the sample re-analyzed. It should be remembered that the observed resolution for a spectrum may vary according to the nuclide's alpha emission decay scheme (e.g., the uranium isotopes have multiple alpha emissions that are very close in energies).

Some improvement in the peak resolution will be observed if the source-to-detector distance is increased. However, this results in a lower counting efficiency and, thus, longer counting times to meet a desired detection level.

15.4.4 Fluorescent Detectors

In a scintillation counter, the alpha particle transfers its energy to a scintillator such as zinc sulfide (silver activated). The energy transfer to the scintillator results in the production of light at a wavelength characteristic to the scintillator, and with an intensity proportional to the energy imparted from the alpha particle. In the alpha counter, the scintillator medium is placed in close proximity to the cathode of a photomultiplier tube (PMT) where light photons from the scintillator strike its photocathode, and electrons are emitted. The photoelectrons are passed through a series of dynodes resulting in the multiplication of electrons at each stage of the PMT. After amplification, a typical scintillation event will give rise to 10^7 to 10^{10} electrons, which is sufficient to serve as a signal charge for the scintillation event. The electrons 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 alpha counter size is typically limited by the PMT size, with the most common having a diameter of 51 mm. Two types of systems may be employed. In the first, the phosphor is optically coupled to the PMT and is either covered with a thin (<1 mg/cm^2) opaque window or enclosed in a light-proof sample changer. With the test source placed as close as possible to the scintillator, efficiencies approaching 40 percent may be obtained. The second system employs a bare PMT housed in a light-proof assembly. The test source is mounted in contact with a disposable zinc sulfide disk and placed on the PMT for counting. This system gives efficiencies approaching 50 percent, is associated with a slightly lower background, and less chance of counter contamination.

Other than for analyzing ^{226}Ra, alpha-scintillator detectors have a limited application and are not used routinely in most radioanalytical laboratories. However, a major advantage of alpha scintillation counting is that the test source or mount need not be conducting. However, they are used extensively in remote laboratory locations for health physics applications that involve the measurement of alpha activity on air particulate filters and swipes. Commercially manufactured portable survey detector counting systems are available for these applications.

15.4.4.1   Zinc Sulfide

Silver-activated zinc sulphide is the most commonly used inorganic scintillator for alpha-particle counting. ZnS(Ag) has a wavelength of the maximum photon emission of 450 nm and a decay constant of 0.25 μs (Knoll, 1979). For practical purposes, the preamplifier/amplifier time constants should expect a pulse duration of 10 μs (Watt and Ramsden, 1964). Compared to other inorganic scintillators such as NaI(Tl), ZnS(Ag) has a very high scintillation efficiency.

ZnS is available only as a polycrystalline powder, which limits its application to various detector configurations. In addition, light transmission through thicknesses of 25 mg/cm^2 thickness becomes limited because of the opacity of the multicrystalline layer to its own luminescence (Knoll, 1979).

DETECTOR REQUIREMENTS AND CHARACTERISTICS

An alpha counting system consists of a ZnS(Ag)-phosphor transparent screen and a PMT housed in a light-tight housing coupled to a preamplifier/amplifier/scaler counter. As a precaution, the housing for the PMT should be made with a voltage cutoff switch to remove the high voltage from the PMT when the housing is opened. It is desirable to have a separate screen coated with the ZnS(Ag) rather than coating the PMT with the phosphor. The glass on the PMT has inherent naturally occurring nuclides that may increase the background by as much as a factor of two. Laboratories can fabricate their own detector screens by spraying the ZnS(Ag) phosphor as a pigment onto one side of a Mylar™ film (HASL 300, DOE 1997). ZnS(Ag) may be obtained as a Sylvania Type 130® or Dupont 1101® phosphor. Different batches of ZnS(Ag) may vary in characteristics and inherent background. As such, it is recommended that each batch be tested before use. A thin (clear) Persex® sheet material has been used in addition to the Mylar™. Other techniques for fabricating ZnS(Ag) phosphor screen have been reported by Watt and Ramsden (Watt and Ramsden, 1964).

Previously, phosphor screens were commercially available as discs (24, 49, or 51 mm diameter) or 305 mm wide strips. However, because of the recent low demand for their use, the commercially available source supply for the phosphor screens is limited (vendors can be found by conducting an the Internet search for "ZnS scintillator screens"). ZnS(Ag) screens are commercially available in 216×279 mm sheets and two sizes of discs (47 to 50.8 mm diameter and 38 to 44 mm diameter).

The ZnS(Ag) thickness on the phosphor screen is typically between 8–16 mg/cm^2. Thicknesses greater than 10 mg/cm^2 do not enhance the detection efficiency of the phosphor screen since the alpha particles from most naturally occurring nuclides are absorbed in this thickness (Watt and Ramsden, 1964). In addition, it is most desirable to limit the thickness of the phosphor screen in order to reduce any inherent background from the ZnS(Ag).

In one application for alpha-gamma coincidence counting of the radium isotopes, a small amount of ZnS(Ag) powder was added to a solution of suspended Ba(Ra)SO$_4$, filtered (0.4 μm pore size), and dried. The filter paper was mounted on a 25.4 mm diameter plastic mount, covered with a thin clear Mylar™ sheet, and counted on a PMT. Maximum alpha particle detection efficiency was obtained when the ZnS(Ag) to BaSO$_4$ mass ratio was about 2.4 for a typical final counting mass of about 64 mg, or about 13 mg/cm^2 (McCurdy and Mellor, 1981). This phosphor/test-source configuration has the advantage of a nearly 4π geometry efficiency and a low background.

OPERATING VOLTAGE

The operating high voltage of the ZnS counting system varies according to the size and characteristics of the PMT employed and the voltage discriminator setting of the scaler unit. The operating voltage is determined by developing a voltage versus count rate curve for a calibrated source. Similar to a gas proportional counter, a voltage plateau will be observed after a certain applied voltage. A system having a 89 mm (3.5 inch) diameter PM tube and a plateau length of 200 V DC was reported having a 2–3 percent slope per 100 V DC (PHS, 1967b). The operating voltage is selected at stable point above the knee of the voltage plateau. The voltage plateau will vary according to the PMT size. However, most PMTs for this application will be operated below 2,000 V DC.

SHIELDING

A ZnS(Ag) alpha detection system is normally constructed and operated without shielding from cosmic or terrestrial radiations. The lack of a shielding requirement simplifies the fabrication of a light-tight PMT housing and the cost of the system.

BACKGROUND

In general, the background of an unshielded ZnS(Ag) detector counting system is quite low. For an unshielded thin layer of ZnS(Ag) on a thin plastic disc responding to an energy range of 0.1 to 6 MeV, the background is between one and a few counts per minute. For a 51 mm PMT with the phosphor coupled to the tube, typical background values of 0.006 cps may be obtained. With a disposable phosphor mounted on the test source, a background count rate of 0.003 cps can be obtained.

15.4.4.2   Calibration- and Test-Source Preparation

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 PMT and counted. Because of the availability of large PMTs, sources up to 5 inches (12.5 cm) in diameter can be prepared for measurement (PHS, 1967a). Thin and thick test sources may be analyzed with a phosphor screen scintillation counter. Infinitely thick test sources have been analyzed for ^{226}Ra and decay products by a scintillation counter (NCRP, 1978). A filter or planchet mount may be used for radiochemical methods that use coprecipitation or precipitation as the final product, e.g., radium isotopes with $BaSO_4$. Because the alpha particle emitted from a source interacts with the phosphor screen, as it does with an internal proportional counter, the description concerning self-absorption and scatter of alpha particles during analysis in a proportional counter (see Section 15.4.2.2 on page 15-25)

may be applied to counting source mounts 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 test source may be prepared by mixing ZnS(Ag) with a precipitate containing the alpha-emitting nuclide. In an application for isotopic radium analysis (McCurdy and Mellor, 1981), a test-source mount was prepared by sandwiching a mixture of $Ba(Ra)SO_4$ precipitate and ZnS(Ag) on a filter paper between two Mylar™ sheets on a Spex™ counting mount. The counting mount was placed on a small PMT and count for alpha activity. This phosphor-test-source configuration can result in almost 100 percent counting efficiency if the precipitate and phosphor mass ratio is properly maintained, and the total test-source mass kept below about 15 mg/cm^2.

15.4.4.3   Detector Calibration

A ZnS(Ag) alpha detection system may have an efficiency for an electrodeposited calibration source of 45 to 50 percent. The considerations related to calibrations discussed for proportional counters (Section 15.4.2.3) apply equally to a scintillation counter calibration. A basic difference between alpha particle scintillation counting and GP counting is the final calibration/test-source mounting scheme. In order to take advantage of the high efficiency of detection, the source mount should be placed against the ZnS(Ag) screen and coupled to the PMT. Only certain mounting schemes permit such source mount configurations. A source/phosphor screen adhered to or inserted into metal planchet typically used for GP counting can be also be used.

15.4.4.4   Troubleshooting

Since the alpha scintillation counting system is relatively simple, problems related to the electronic components are easily evaluated with an oscilloscope. Lack of signal may be from a PM tube failure, loss of detector bias voltage, or a malfunction of a preamplifier or amplifier. Care should be taken to ensure that the PM tube is protected from physical abuse or exposure to the light while operating. Most scintillation counting systems will have an electrical interlock on the detector bias supply that will be activated (removes bias from the detector) when the light-tight PMT housing is opened or removed.

Problems encountered with the preparation of calibration and test sources for alpha particle scintillation counting are similar to those for gross alpha counting by gas proportional counters. Nonuniformity of the phosphor on a scintillation screen as well as the possible variability in the counting efficiency of the individual scintillator screens within a production batch may cause variability in the test-source results.

15.4.5 Photon Electron Rejecting Alpha Liquid Scintillation (PERALS®)

The PERALS spectrometry system 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 test-source/scintillation cocktail. PERALS® is unique because of its specifically fabricated test-source/detector geometry configuration that uses a silicone oil light-coupling fluid between the PMT face and a test source (10×75 mm borosilicate glass culture tubes). McDowell (1992) provides a complete description and some radioanalytical applications of the PERALS system. A 0.5 MeV beta particle and a 5 MeV alpha particle will produce approximately the same amount of light in the scintillator and thus the same voltage pulse height. However, the alpha generated voltage pulses decay much slower than a beta produced voltage pulse. This is because the alpha particle energy deposition takes the fluor to a triplet excited state. Typically, beta particles deposit energy such that the fluor only is excited to the singlet state, which undergoes rapid decay. The de-excitation from triplet state takes about 35 ns. Thus, the beta and alpha pulses can be differentiated. Once the PMT voltage pulses are amplified and shaped, the decay of the light-generated voltage pulse is evaluated, and an analog output pulse is generated that is proportional to the decay of the light produced by the particle. Rejection of the beta–gamma spectrum is accomplished by setting a 10-turn-potentiometer pulse-shape discriminator (PSD) below the alpha spectrum as acquired from the "pulse shape" spectra. In order to reject exceeding large output voltage pulses, a voltage pileup rejection potentiometer is set. The output pulse is fed to a MCA or an ADC/computer combination.

Many laboratories have had success using the PERALS counting system in conjunction with the use of extractive scintillators cocktails that are readily available. Dacheux and Aupiais (1997) presented an evaluation of the PERALS counting system in comparison to typical alpha spectrometry for ^{232}Th, $^{234/238}$U, ^{237}Np, $^{238/239}$Pu, $^{241/243}$Am and $^{244/248}$Cm in aqueous solutions. The authors found that the PERALS extractive scintillator method equaled or bettered detection limits for the nuclides evaluated compared to alpha spectrometric methods.

15.4.5.1   Detector Requirements and Characteristics

PERALS can be a stand-alone unit or mounted into a triple width standard nuclear instrumentation module (NIM). The unit requires an external or optional internal DC power supply (~ mA) for operation with a photomultiplier tube. PERALS also requires an external multichannel analyzer (MCA) or an ADC with computer combination. The PERALS output is connected to the MCA or ADC for spectrometry applications. The unipolor output pulse is less than + 10 V (adjustable) and has a dwell time of 1.5 μs. Typical alpha peak resolution typically is less than 300 keV (FWHM) or about 5 percent when used in conjunction with extractive scintillators formulated for a number of radionuclides of interest. Dewberry (1997) has reported a PERALS system FWHM resolution of 130 keV for uranium analyses using URAEX® extractive scintillator.

OPERATING VOLTAGE

The PERALS NIM module has an optional internal high-voltage power supply that provides bias to the detector. The operating voltage is normally +500 V DC. An external power supply may be used if the power supply can provide 1 mA at the required +500 V DC. Circuitry is provided for both internal and external bias supply options to disable the high voltage from the PMT when the sample chamber is opened.

SHIELDING

As with other alpha particle detectors, there is no need for substantial shielding from cosmic and terrestrial radiations. The PERALS® unit mounts in a standard unshielded NIM or an aluminum case. However, the manufacturer uses "mu-metal" (Ni-Fe-Mo alloy) to shield the PMT from external magnetic interference.

BACKGROUND

The PERALS unit exhibits excellent detector background characteristics. Normally, the detector background of a scintillator for the 4.0 to 7.0 MeV energy range is about 0.00002 cps (0.001 cpm) with high purity extractive scintillators without reagents. For the same energy range, a reagent background is about a factor of ten higher.

As a result of the low background achieved and a detection efficiency near 100 percent, the figure of merit (efficiency^2/background) and minimum detectable activity are better for the PERALS system compared to other types of alpha particle counting units. Typical detection limits for the alpha emitters may range from 0.0005–0.024 Bq/L depending on the sample volume, interferences and counting time of the test source.

DARK ADAPTATION OF SOURCES

Test sources prepared in a recommended extractive scintillator and counted in a PERALS system do not have to be dark adapted prior to the measurements. The liquid scintillation cocktail selected by the manufacturer, (e.g., PBBO* scintillator in toluene) does not have the normal light sensitivity/luminescence characteristics found in other cocktails used by a typical liquid scintillation counting system.

CHANNEL OVERLAP

In a typical commercial liquid scintillation counting system that distinguishes between alpha and

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* 2-(4'-biphenylyl) 6-phenylbenzoxazole

beta particle interactions in a cocktail by voltage pulse height, there may be alpha pulses registered as beta pulses and vise versa. This false registration of the alpha or beta pulses is known as "crosstalk." Normally, crosstalk becomes more severe as the level of quenching of the test-source increases (see Section 15.4.5.4, "Quench"). As a result of the photon-electron rejection circuitry, voltage pulses from beta particles and photon-generated electrons are not registered (less than 0.1 percent) and cannot overlap into the alpha pulse region.

15.4.5.2   Calibration- and Test-Source Preparation

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). 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 emitting nuclide in an aqueous sample is extracted into an organic extractant–scintillator mixture and counted by the PERALS system.

A manufacturer has combined an organic extractant with a scintillator to produce six cocktails that can be used for a variety of alpha emitting nuclides and counted by a liquid scintillation counter, preferably the PERALS. A specific method for uranium in drinking water using an extractive scintillator and the PERALS system has undergone an interlaboratory comparison study that has been published by ASTM as D6239. The PERALS system had sufficient spectral resolution to resolve the alpha peaks of ^{234}U and ^{238}U and to estimate the ^{234}U : ^{238}U activity ratio. In addition, a ^{232}U yield tracer may be resolved. Duffey et al. (1997) have published a detailed method for the analysis of uranium in drinking water using the PERALS system that includes the results of the ASTM method.

Dacheux and Aupiais (1997), in their evaluation of the PERALS® counting system in comparison to typical radiochemistry: alpha spectrometry for ^{232}Th, $^{234,/238}$U, ^{237}Np, $^{238, 239}$Pu, $^{241/243}$Am, and $^{244/248}$Cm in aqueous solutions used the extractive scintillators of ALPHAEX $_\alpha$®, URAEX $_\alpha$® and THOREX $_\alpha$®. The authors provide a sequential method of separating the thorium, uranium, plutonium, americium, neptunium, and curium elements, including the oxidation-reduction steps for proper elemental extraction into the extractive scintillators. A similar study for ^{239}Pu in aqueous solutions using ALPHAEX $_\alpha$ and THOREX $_\alpha$ was reported by Aupiais (1997). Using the method described, a detection limit of 4.8×10^{-4} Bq/L was quoted for a 24 hour counting interval and a 250 mL sample. Recommendations as to use of tracers for ^{232}Th, $^{234/238}$U, $^{238,/239}$Pu and $^{244/248}$Cm are provided based on the ~ 300 keV alpha peak resolution of the instrument.

Escobar et al., has used the RADAEX $_\alpha$® extractive scintillator cocktail for the analysis of ^{226}Ra in water samples by a typical (non-PERALS) LS counting system (Escobar et al., 1999) for sample volumes greater than 19 mL. The authors followed the manufacturer's recommendations for sample preparation prior to extracting the radium into the extractive scintillator. Sample dissolved radon interference, which is extracted with the radium, was eliminated by heating and

stirring the samples for one hour at 60 °C. Accurate results were obtained for ^{226}Ra concentrations in the range of 0.38–2.36 Bq/L in the presence of ^{230}Th and ^{210}Po added interferences. A detection limit of 0.024 Bq/L was quoted for a one liter sample and a 12,000 s counting time.

In addition to the use of PERALS® for the analysis of the long-lived alpha emitting radionuclides in water, other reported applications include high-level waste samples (Dewberry et al., 1998) and airborne uranium (Metzger et al., 1997). Additional references to radioanalytical methods may be obtained from the manufacturer.

15.4.5.3   Detector Calibration

The settings and calibration of a PERALS unit are established by the manufacturer prior to delivery. The calibration is performed using a ^{226}Ra reference source (with cocktail) so that the 6 MeV ^{218}Po alpha particle produces a 6 volt output pulse for input into an analog-to-digital convertor/computer or multichannel analyzer. A detection efficiency of about 99 percent and a FWHM resolution less than 300 keV can be obtained for most applications when calibrated. If a tracer is to be used, the alpha energy of its emission should be sufficiently different from the alpha energy of the nuclide of interest to prevent peak interferences requiring corrections, e.g., greater than 700 keV.

15.4.5.4   Quench

Two types of quenching may be encountered in liquid scintillation counting: chemical or color quenching. Color quenching results in a reduction of the scintillation intensity (as seen by the photomultiplier tubes) because of absorption of the fluor scintillation by colored materials present in the cocktail. This results in fewer photons per quanta of particle energy reaching the PMT and a reduction in counting efficiency. Chemical quenching results in a reduction in the scintillation intensity because of 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.

In order to minimize the effects of oxygen quenching, the test-source/scintillation-cocktail combination is sparged with toluene-saturated argon. The manufacturer has developed methods or recommends methods that minimize color quenching of the test sources. The ferric ion is a known color-quenching agent (also for the standard LSC and LS cocktails) that shifts the energy spectrum to a lower energy. A yellow test-source color exhibits the most color quenching. Removal of the Fe^{+3} ion or reducing it to Fe^{+2} (e.g., addition of ascorbic acid) prior to the addition of the extractive scintillator to the sample is recommended. The Fe^{+2} ion is not extracted into the extractive scintillator.

In order to determine the extent of any color quenching, a test-source spectrum should be compared to a spectrum obtained from spiking the extractive scintillator with the nuclide of interest.

15.4.5.5   Available Cocktails

Currently, six proprietary extractive scintillators are available to the user for analyzing the more important long-lived naturally occurring or manmade alpha emitting nuclides. The commercially available extractive scintillators include: $ALPHAEX_\alpha^®$, $POLEX_\alpha^®$, $RADAEX_\alpha^®$, $THOREX_\alpha^®$, and $URAEX_\alpha^®$. In addition to the above elements, the extractive scintillator $RADON_\alpha^®$ also has been developed for radon. The extractants used usually have distribution coefficients greater than 1,000. The quantitative recovery of a nuclide in a test solution will depend on both the distribution coefficient and the volume ratio of extractive scintillator to aqueous solution. The use and selection of the extractive scintillator is based on the valence state of the nuclide in the test solution. Controlled aqueous ionic phase conditions must be established to ensure maximum nuclide extraction and unquenched counting conditions. These conditions vary considerably from an acidic media, an acidic sulfate media, or a basic nitrate media.

15.4.5.6   Troubleshooting

The manufacturer has provided a troubleshooting section within the instrument instruction manual that primarily deals with the electronic aspects and setup of the PERALS® spectrometer. In addition, the manual contains several sections on sample preparation, radiochemical procedures, alpha-emitting nuclide measurements, coincidence measurements and theory of operation. Not all of the items discussed in Section 15.5.3.4 on liquid scintillation counting troubleshooting apply to PERALS® because of its uniqueness (e.g., LS cocktail dark adaption). However, certain aspects of LS sample quenching apply to both applications even though sparging of the test-source/LS cocktail with toluene-saturated argon is unique to PERALS. Specific information on troubleshooting of the procedures and instrumentation can be obtained from the manufacturer.

15.5 Beta Detection Methods

15.5.1 Introduction

Radioactive decay by beta particle emission is generally accompanied by one or more gamma-ray emissions; the latter normally is much easier to identify and quantify. Beta-particle counting typically is more difficult, because of the additional source preparation and associated complications resulting from the effects of backscatter, scattering, and absorption in the source material (NAS/NRC, 1962). Since beta particles are not emitted monoenergetically, there is additional difficulty in obtaining quantitative measurements. Guidance on beta particle counting can be found in industry standards (ASTM D1890; D3648; E1329) and publications (NCRP, 1978; Knoll, 1989; Lapp and Andrews, 1964; Price, 1989; PHS, 1967a; Mann et al., 1991; Wang and Willis, 1965; Watt and Ramsden,1964).

Accurate beta-particle measurements will depend upon the degree and extent to which the various parameters that affect the measurement process under considerations are evaluated. For beta particle counting, the items that should be considered include:

- Beta-particle energy or energies, including conversion electrons;
- Radiation detector characteristics;
- Material and geometry (including source-to-detector distance) of the final source mount;
- Form and thickness of final source for analysis; and
- Radionuclide purity of final source.

For certain beta-detection methods, beta-particle attenuation in the air/detector window, self absorption and backscatter corrections to the detector efficiency may be necessary depending on the beta-particle energy, detection system and final source form. Various beta-detection systems, such as liquid scintillation, have been developed to minimize the need for such corrections but these systems may have characteristics that require other type of detector efficiency corrections, e.g., color or chemical quenching. The potential of detector contamination from test-source measurements is a function of the type of detector used and the stability of the final test-source composition. The inherent beta-particle background of the various detection systems should be evaluated and its contribution removed from the test-source measurement result. Many of these items are discussed in Sections 15.2 and 15.3 on the preparation of sources.

The radiation detectors used for beta-particle measurements include an end window Geiger-Mueller tube, gas proportional chamber, liquid scintillation counter, plastic scintillators, and solid-state detectors. Each of these detectors is discussed in subsequent subsections. The end window Geiger-Mueller tube, plastic scintillators, and solid-state detectors have limited laboratory applications for beta-particle detection. Since the end-window Geiger-Mueller tube and gas proportional counters have similar characteristics and operational requirements, these two beta-particle detectors are discussed in the same subsection.

"Gross" beta counting of evaporated samples, wherein a multitude of 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. This 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 test-source form and the range of final test-source masses expected from

chemical recovery.

The beta particle measurement system should be calibrated with standards traceable to a national standards body such as NIST and its subsequent performance held to established measurement quality requirements through the use of instrument QC checks (Section 18.5.6, "Summary Guidance on Instrument Calibration, Background, and Quality Control"). In addition, appropriate instrument QC should be established for background, voltage plateau, quenching, resolution, and alpha-beta crosstalk (Section 18.5.4.2, "Self-Absorption, Backscatter, and Crosstalk").

Certain aqueous beta-emitting radionuclide calibration standards and sources are available from NIST or from a radioactive source manufacturer (complies with ANSI N42.22) that supplies NIST-traceable standards. 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. Refer to Table 15.4 for the availability of known beta-emitting radionuclides. Contact a radioactive source manufacturer that supplies NIST-traceable standards for the availability of other pure beta or beta/gamma-emitting radionuclides (ANSI N42.15).

TABLE 15.4 — Nuclides for beta calibration

Purpose	Nuclide	Reference
Specific Nuclide Analyses	^{3}H, ^{14}C, ^{63}Ni, ^{89}Sr, ^{90}Sr (also ^{90}Y), ^{99}Tc, ^{129}I, ^{131}I, ^{228}Ra (also ^{228}Ac), and ^{241}Pu	Various Methods
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/Y	APHA (1998), Method 7110

Beta detectors should be calibrated according to their intended use, i.e., nuclide specific or gross beta measurement applications. An example of detector calibration for the specific radionuclide of ^{90}Sr can be found in ASTM D5811. Gross beta measurements, as the name implies, are non-specific to a given beta-emitting nuclide and typically require no chemical separations or purification steps. The most common applications for gross beta measures are health physics swipes for contamination surveys, air particulate filter papers from air monitoring programs, and evaporated surface or ground water onto a metal planchet. For gross beta-particle measurements, the instrument's calibration is related to a reference nuclide, typically one that is specified by a laboratory client, measurement quality objectives, or by regulatory requirements. Typical beta-emitting reference nuclides for gross beta analyses include ^{137}Cs, ^{90}Sr/Y, ^{99}Tc, or ^{40}K. Table 15.4 lists beta emitting calibration standards for beta analysis referenced in various national standards.

Aqueous radioactive standards can be prepared in the appropriate geometry for LS or Cerenkov counting or through chemical processing, precipitated, electroplated, or evaporated as a final test-

source form for counting by a GP, plastic, or solid-state beta-detection system.

15.5.2 Gas Proportional Counting/Geiger-Mueller Tube Counting

The end-window Geiger-Mueller (GM) tube and the GP counting chamber are the two most prevalent types of detectors used for field and laboratory beta particle counting applications. However, because of its dual use for alpha and beta particle counting, the GP (chamber) counter is used almost exclusively by radioanalytical laboratories. The end-window GM tube counter cannot differentiate between alpha and beta particles because of its operating characteristics. In other words, the total number of ion pairs produced to generate a voltage pulse is independent of the primary ionization (alpha or beta particle interaction), which initiated the detection event. The end-window GM counter is typically used with a survey meter for field or laboratory applications such as the beta measurements of surface contamination, health physics swipes, air filters and soil measurements. Several types of commercially available GP counters are described in Section 15.4.2, on page 15-20.

15.5.2.1   Detector Requirements and Characteristics

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 test source by an overall efficiency factor. This factor combines the effects of test-source-to-detector geometry, test-source 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 test-source specimen, or an arbitrary efficiency factor can be defined in terms of a single calibration source, such as ^{137}Cs or another 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.

For both window-type gas proportional and end-window GM counters, the thickness of the detector window should be selected to reduce transmission losses from beta particle absorption in the window. The severity of the beta absorption in the window is a function of beta-particle energy and window material and thickness. Estimates of the transmission of beta particles through GM tube walls and windows have been evaluated by Price (1964). These transmission loss estimates are also applicable to the thickness of a window on a GP detector. For ^{14}C with a maximum beta energy of 154 keV, the transmission through a 4 and 0.9 mg/cm^2 window thickness would be approximately 35 and 79 percent, respectively. For the same window thicknesses, the transmission of beta particles from ^{64}Cu with a 580 keV E$_{\beta max}$ would be about 87 and 97 percent, respectively. Most commercially available gas proportional counters offer detector windows that are thinner than 0.09 mg/cm^2 (e.g., 0.08 mg/cm^2).

Various GP counter characteristics, including detector size, counting gas, window thickness, restrictions on size of test-source mounts, etc., are presented in Section 15.4.2.1. Typical values for the important operational parameters for GP beta-particle counting are provided in Table 15.5.

TABLE 15.5 — Typical operational parameters for gas proportional beta counting

Background count rate	24–50 counts/hour (0.007 to 0.014 cps)
Length of voltage plateau	200 V DC using P-10 gas
Slope of voltage plateau for well-designed detector	2.5%/100 V DC for an electroplated source
Windowless detector efficiency $- \dfrac{100 \times \text{count rate}}{\alpha \ \text{emission rate}}$	$\leq 60\%$ for an electroplated ^{90}Sr/Y source including backscatter
Windowed efficiency (0.5 mg/cm^2 thickness) $- \dfrac{100 \times \text{count rate}}{\alpha \ \text{emission rate}}$	$\leq 45\%$ for an electroplated ^{90}Sr/Y source including backscatter

At least one instrument manufacturer has engineered a windowless GP counter available as either a sequential multiple sample (test source) GP counters and multiple detector single sample (test source) GP counters. The units available typically have lower beta background and higher detector efficiency specifications compared to the windowed GP counters.

SHIELDING

Most GP systems used for beta particle measurements have shielding to reduce the beta background count rate. Shielding reduces the beta background by absorbing some of the components of cosmic radiation and radiations emitted from materials in the surroundings of the measurement system. Ideally, the material used for the shielding should itself be free of any radioactive material that might contribute to the background.

Commercially available low-background GP systems typically have 102 mm of lead surrounding the test-source and cosmic-guard (anti-coincidence detection system) detectors. For a sequential sample GP counting system, the lead shielding may weigh several hundred kilograms depending on the shielding configuration. With the shielding included, a sequential sample GP counting system may weigh up to 360 kg. Portable GP counting systems with less shielding are available but their beta-particle backgrounds are higher.

BACKGROUND

The GP detector's beta background is principally due to the secondary electrons generated from the interaction of cosmic radiation and photon radiations emitted from materials in the surroundings, including the detector shield and housing. Some contribution to the background also may come from beta particles originating in the materials surrounding the detector that may

enter the sensitive volume of the detector.

Most of the commercial GP counting systems have passive detector shielding and active cosmic guard (anti-coincidence counting detectors/circuits) components to reduce a detector's beta background. The efficiency of the cosmic guard to reject coincident high-energy cosmic radiation is greater than 99 percent. The anti-coincidence detector surrounds, or is in close proximity to, the primary counting chamber and detects interaction events that are caused by radiations from cosmic rays and the inherent radioactivity in the building and surrounding materials. The anti-coincidence circuitry prevents detector events from being registered that have occurred simul-taneously in both the primary test-source-counting and coincidence-counting detectors. Without shielding and anti-coincidence counting detector/circuitry, the background of a GP counter operating at the beta plateau would be about 50 cpm.

The beta-particle background for a GP counting system will depend upon detector size. For some commercial units with a 57.2 mm diameter detector and a 0.08 mg/cm^2 window thickness using P-10 gas, the beta-particle background count rate commonly is about 51 counts per hour (0.85 cpm). A background of 24 counts per hour (0.4 cpm) also may be obtained for some commercial units. These background values apply to GP counting systems with passive lead shielding and active cosmic guard background reduction components.

OPERATING VOLTAGE

The operating voltage of a GP counter used in the beta-particle counting mode depends on the counting gas used, the amplifier and voltage discriminator settings, and the mode of beta-particle discrimination, i.e., voltage pulse height discrimination or simultaneous alpha- and beta-particle counting. A generic discussion on these parameters is provided on page 15-23 for GP counting systems .

Prior to the operation of a gas proportional counter, the operating voltage of the detector must be determined in conjunction with the other operating parameters. Normally, the manufacturer of the unit recommends the voltage discriminator and amplifier gains settings. The user typically places an electroplated beta source into the counting position and increases the detector bias voltage in discrete 25 or 50 V DC increments while recording the observed source count rate at each voltage setting. Figure 15.3 illustrates a typical voltage response curve for a commercial window type gas proportional counter detector using P-10 counting gas and a massless ^{90}Sr/Y source (Canberra, 2002). The operating plateau for beta counting is between 1,400–1,600 V DC. For most commercial GP units, the slope of this plateau should be ≤ 2.5 percent per 100 volts over a 200-volt range. When using the separate alpha plateau then beta (plus alpha) plateau counting modes, the alpha count rate on the beta plateau must be determined at the alpha and beta plateau voltages selected during calibration, (i.e., determining the ratio of the alpha-particle count rate on the beta plateau to the alpha-particle count rate on the alpha plateau). For test-source measurements, the observed beta-particle count rate must be adjusted for the alpha-
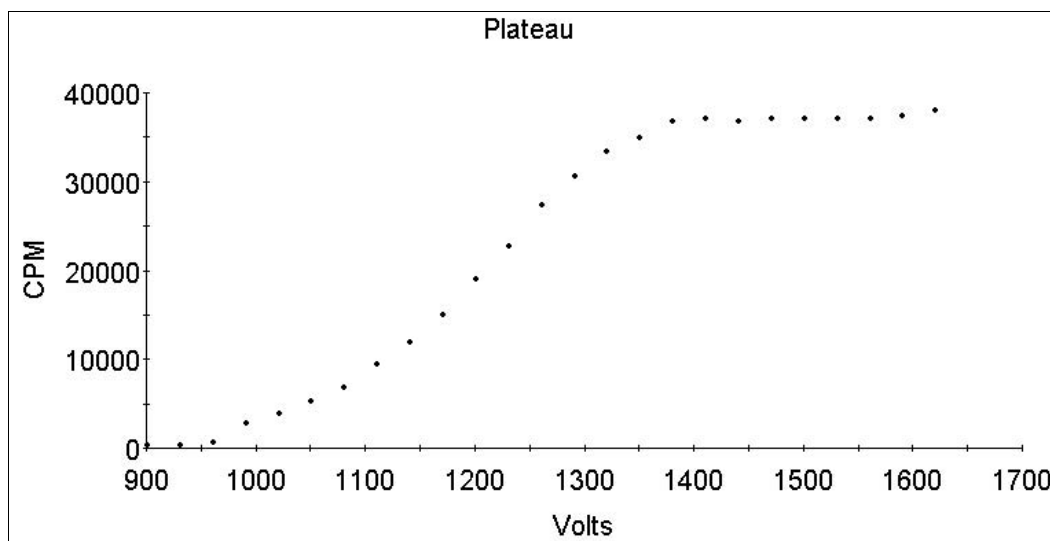
FIGURE 15.3 — Beta plateau generated by a ^{90}Sr/Y source on a GP counter using P-10 gas

particle count rate on the beta plateau by applying a correction factor using this ratio. The observed increase in the alpha-particle count rate on the beta plateau varies according to the alpha-emitting nuclide. The difference between the count rates on the two plateaus will be accentuated for nuclides that have both alpha and photon emissions, e.g., ^{241}Am.

For the simultaneous alpha and beta counting mode, the detector operating voltage is located on the beta particle plateau. For this counting mode, the voltage discriminator setting for alpha detection is set so that only a small fraction (less than 1.0 percent) of the alpha detection events will be registered as beta detection events.

15.5.2.1.4 CROSSTALK — REGISTRATION OF ALPHA PULSES AS BETA PULSES

Modern proportional counters are capable of electronically discriminating between alpha and beta interactions in the detector. As discussed on page 15-24, this differentiation is accomplished by identifying the two types of particles based on the resultant voltage pulse heights from their interactive events in the detector. Those pulses whose heights exceed an experimentally established voltage (pulse) discriminator level are registered as alpha counts and those falling below this level are recorded as beta counts. The dynamic range of the voltage separation between the alpha and beta voltage pulses varies by detector design and manufacturer. If the voltage discriminator is not properly set, a fraction of high-energy beta particles may be recorded as alpha particles. In addition, severely degraded alpha particles, because of their self absorption in a test source of significant masses, may be recorded as beta particles. This missclassification of alpha and beta counts is referred to as "crosstalk." The degree of spillover varies according to detector design and GP counter manufacturer.

For some commercial GP counters, crosstalk may occur for both modes of GP counting, i.e., alpha then beta plateau counting and simultaneous alpha and beta counting. For electroplated beta particle sources, the crosstalk is minimum for both counting modes when the voltage (pulse) discriminator is properly set. However, certain alpha emitting radionuclides [230]Th, [235]U, [238]U, [241]Am, [238]Pu, [239]Pu) have multiple low-energy conversion electron/photon emissions that may be registered as beta particles. The user should review the decay scheme of the nuclide of interest to gain a perspective on the extent of the possible alpha-to-beta crosstalk.

For both counting modes, corrections should be made to the beta count rate to remove the portion contributed by alpha particles. Since the fraction of the alpha counts occurring in the beta channel depends on the source mass, a crosstalk curve should be developed. This can be accomplished concurrently with the self-absorption calibration for the alpha emitting radionuclide selected. A crosstalk response curve is generated by recording the beta counts from the alpha self-absorption determination at all source masses and plotting the crosstalk fraction (alpha-particle count rate in beta channel/alpha count rate in alpha channel) as a function of source mass (Section 17.4, "Data Reduction on Non-Spectrometry Systems"). Beta-particle count rates then can be corrected for the influence of the alpha particles at all source thicknesses.

15.5.2.2 Calibration- and Test-Source Preparation

For specific nuclide beta particle counting by a gas proportional counter, chemical separations are typically performed to isolate the radionuclide of interest from other beta emitting radionuclides. Beta measurements are performed on chemically isolated pure beta emitters (beta decay not accompanied by a gamma-ray) and also in cases when better detection capabilities (increased sensitivity) are required to meet detection limits, such as, ^{89}Sr, ^{90}Sr, ^{99}Tc, ^{131}I, [134]Cs, and [137]Cs (EPA, 1980). Test sources measured in a proportional counter are usually prepared by electrodeposition, coprecipitation, or evaporation (Blanchard et al., 1960). The comments on chemical reactivity of source-contained materials and contamination given in Section 15.3 apply.

Test- and calibration-source preparation techniques and applications for GP counting are presented in Section 15.3. These preparation techniques have been presented in a fairly generic manner but with identification of the applications to alpha and beta counting. Refer to the section for information on preparing test and calibration sources for beta particle radionuclides applicable to gas proportional counting.

Preparation of beta calibration and test sources by precipitation/coprecipitation applicable to gas proportional counting also is discussed in Section 15.3. The techniques include precipitation of the radionuclide with the element of interest (e.g., Cu[131]I) and co-precipitation of a radionuclide with a chemically similar element that forms a precipitate (e.g., $NdF_3 - $ [239]Pu). Table 15.1 (page 15-12) provides a listing of the common precipitates and coprecipitates used for both beta- and alpha-emitting radionuclides.

15.5.2.3   Detector Calibration

Calibrations for beta particle measurements can be accomplished for either the beta (plus alpha) plateau counting mode or the simultaneous alpha and beta counting mode. However, for both modes of operation, calibration sources should be prepared in a manner identical to the method used for test-source mounting. This may include massless or electroplated sources, micro-precipitated (less than 200 μg) sources and low-mass (1–125 mg) sources. For accurate results, beta self-absorption curves (for both operating modes) and crosstalk corrections (simultaneous counting mode) during the source calibration should be developed.

Beta-particle attenuation should be considered for windowed GP 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 test source. Beta-particle air attenuation is a function of the distance between the test source (or sample) and the detector's particle-entrance window. Under most applications for beta-particle counting, this factor typically is insignificant compared to the other sources of beta-particle attenuation. Consideration of the detector's 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 test-source self-absorption for a given application. In most applications, a backscatter factor for the material composition (Z value) of the final test-source mount is included into a combined attenuation-backscatter-efficiency factor or—more simply—the combined detector efficiency correction factor.

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 test-source 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 test-source matrix and the beta energy of a surrogate. For this reason, using an 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 test-source results, as appropriate. For electroplated plated test sources, a correction factor needs to be determined if the plating material of the surrogate is not the same as that used for the test sources.

Certain aqueous beta-emitting radionuclide calibration standards and sources are available from NIST or from a commercial radioactive source manufacturer that complies with ANSI N42.22. Refer to Section 15.4 for the availability of known beta/gamma-emitting radionuclides. Contact a radioactive source manufacturer for the availability of other NIST-traceable pure beta- or beta/gamma-emitting radionuclides (ANSI N42.15).

The counting efficiency (ε) is determined by counting a calibration source to accumulate sufficient net counts (approximately 10,000) to provide a relative (1σ) counting uncertainty of

about 1 percent and dividing the resultant net count rate (cps) by the beta-emission rate of the source (β/s). The beta emission rate is determined by the source activity (Bq) times the beta abundance per disintegration.

$$\varepsilon = \frac{\text{Measured Net Count Rate (cps)}}{\text{Bq} \times \text{fractional } \beta \text{ abundance}}$$

For a nuclide specific or reference nuclide counting efficiency, the same equation is used but without the beta abundance factor. The uncertainty of the detector efficiency factor can be calculated using the methods described in Chapter 19.

For health physics swipes and air particulate filter samples, a calibration source is prepared by spiking an unused filter with the appropriate calibration solution. For health physics swipes, the entire surface of the filter may be spiked. However, only the active area of an air filter is spiked with the calibration solution. The retainer ring and gasket holding down the filter determines the active area to be spiked. Depending on the filter composition (e.g., glass fiber filter), the filter matrix may cause some wicking of the solution away from the surface. In order to prevent the wicking effect, the surface of the filter may be sprayed with an acrylic lacquer and dried prior to spiking the surface.

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 et al., 1981; Tsoulfanidis, 1983). If test sources of varying mass are to be counted for beta activity determination, a self-absorption curve should 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.

Instrument calibration for a specific nuclide measurement should be calibrated with the radionuclide of interest. In some cases, a radionuclide whose beta emission has the same energy as the nuclide of interest may be used as long as the self-absorption characteristics are similar. An example is the calibration of the GP counter for ^{228}Ac ($\beta_{avg} = 404$ keV) by using ^{89}Sr ($\beta_{avg} = 589$ keV) (EPA, 1980).

In cases where finite test-source thicknesses are unavoidable, beta-source measurements can be adjusted to account for self-absorption (PHS, 1967a). Typical applications for such self-absorption curves include SrCO$_3$ (^{89}Sr and ^{90}Sr), Cu^{131}I, and gross-beta analysis. In order to determine the change in counting efficiency as a function of source thickness or mass, a self-

absorption curve should be developed. Calibration sources containing a known amount of the radionuclide of interest are prepared in varying thicknesses (mass) and counted. Self-absorption curves for gross beta-particle measurements are constructed most frequently using reference material containing ^{137}Cs, ^{90}Sr/Y, ^{99}Tc, or ^{40}K. The self-absorption curve is constructed by counting planchets containing varying mass of material but with a known amount (sometimes constant) of added radioactivity. A discussion on the preparation of a self-absorption curve that relates the self-absorption factor to a zero-thickness efficiency is discussed in Section 15.4.2.3, "Detector Calibration." Most radioanalytical laboratories generate a self-absorption curve by determining the counting efficiency as a function of source mass in milligrams or mg/cm^2 without normalization to the "zero thickness" efficiency. Test sources prepared for gross beta measurement are counted in the exact geometry as those used to prepare the absorption curve. The material forming the matrix for the self-absorption calibration source should, when possible, be identical to that expected in the test sources to be analyzed. For the lower to intermediate beta particle energies, the detector efficiency factor is a function of beta energy, final sample mass and source composition. For beta particles having a maximum beta energies greater than 1,500 keV, the detector efficiency factor is nearly constant over a final sample mass range of 0 to 5 mg/cm^2. For sufficiently thick sources, the number of beta particles interacting with the detector will reach a limit and the count rate becomes independent of the source thickness.

Figure 15.4 illustrates a typical self-absorption curve for ^{90}Sr/Y in a dry residue generated from evaporated tap water. Note that this self-absorption curve is multi-component, where the resulting curve is a composite of the self-absorption effects of the low-energy ^{90}Sr (E$_{\beta max}$ = 546 keV) and the high-energy ^{90}Y (E$_{\beta max}$ = 2.28 MeV).
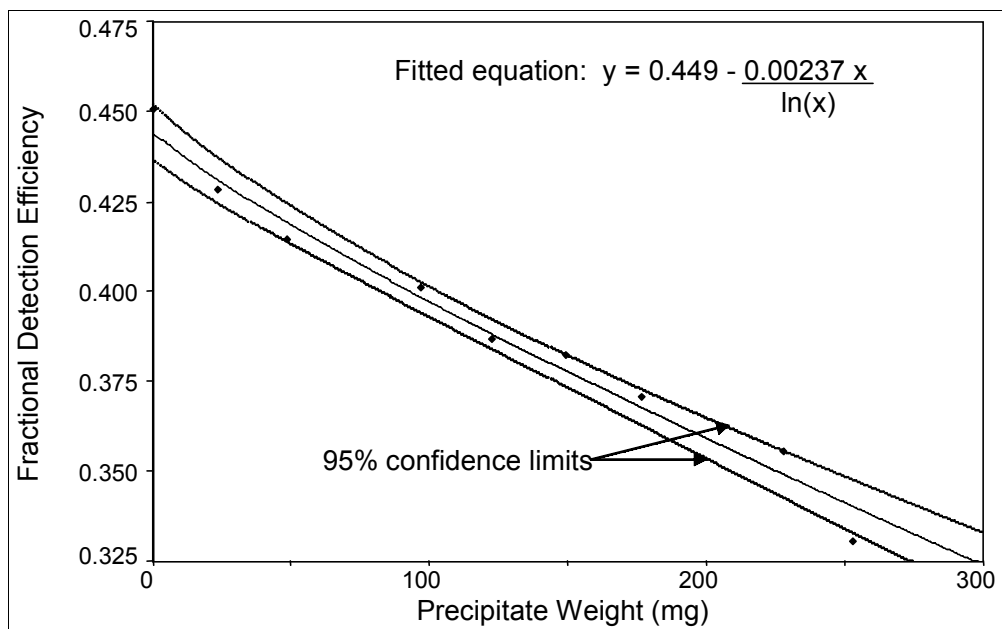
FIGURE 15.4 — Gas proportional counter self-absorption curve for ^{90}Sr/Y

15.5.2.4.   Troubleshooting

Various problems that may arise when counting calibration or test sources on a GP counter are discussed in Section 15.4.2.4. These may include both instrumentation- and test-source preparation related issues. Instrumentation related problems should be identified through the instrument's operational quality control checks that include periodic detector response and background measurements. Section 18.5.6 ("Summary Guidance on Instrument Calibration, Background, and Quality Control") in Chapter 18 provides guidance on the frequency for these types of QC measurements for a GP counter.

Inaccurate results can occur from the misuse of a specific nuclide detector calibration or if the test sources are prepared differently than the calibration sources. It is important that a laboratory and its client cooperatively decide on the nuclide of interest for gross beta measurements as well as the chemical composition of the self-absorption curve that may be used. Some clients may want the laboratory to use the gross beta reference nuclide that the nationally recognized performance evaluation programs incorporate into their gross-alpha test samples. Inaccurate results also will occur when a beta-detector efficiency factor for a massless calibration source is applied as the detection efficiency for air particulate filter or swipe test sources. These test sources normally have some amount of radioactivity/particle penetration into the fibers of the filter or swipe material and may contribute to self absorption depending on the beta energy.

15.5.3 Liquid Scintillation

When beta measurements involving pure beta emitters of low energy are required, they are often performed using liquid scintillation spectrometry, because sample preparation is easy and counting efficiencies are relatively high (Herpers, 1986). Although it is the preferred method for measuring low-energy, pure beta-emitting radionuclides, (e.g., ^{3}H, ^{14}C, ^{35}S, and ^{63}N) it is a well-established procedure for measuring numerous other beta-emitting radionuclides, including ^{45}Ca, ^{32}P, ^{65}Zn, ^{141}Ce, ^{60}Co, ^{89}Sr, ^{55}Fe, ^{87}Rb, ^{147}Pm, and ^{36}Cl (Hemingway, 1975).

Liquid scintillation counting (LSC) avoids many sources of error associated with counting a solid source, such as self-absorption, backscattering, loss of activity during evaporation because of volatilization or spattering, and variable detection efficiency over a wide beta-energy range. In addition to the improvement in the detection capability offered by LSC over other beta counting techniques, sample preparation time and counting times may be significantly shorter. Sample preparation involves only adding a soluble or dispersable sample aliquant to a scintillation cocktail to form a liquid test source. Because every radioactive atom is essentially surrounded by detector molecules, the probability of detection is quite high. Radionuclides having maximum beta energies of 200 keV or more are detected with essentially 100 percent efficiency. Liquid scintillation can, at times, be disadvantageous because of chemiluminescence, phosphorescence, quenching, or high backgrounds (especially in older instruments). However, better coincidence circuitry and use of certain types of shielding (e.g., bismuth germanate) have been able to reduce

backgrounds in newer instruments.

The observed count rate for a liquid-scintillation test or calibration source is directly related to the beta (plus conversion electron) or positron emission rate in most cases. The important exception is beta emitters whose maximum energy is below 200 keV. Low-energy beta emitters, such as tritium (^{3}H, $E_{\beta max}$ = 18 keV) or ^{14}C ($E_{\beta max}$ = 156 keV), have a significant number of emissions that have energies in the range of 0.7 to 4 keV. Beta-particle energy is converted to photons through interaction with the solvent and fluor. It takes about 150 eV to produce one photon. Thus, a 150 keV beta particle will produce about 1,000 photons. These photons are then detected by the PMTs in the LSC instrument. The PMTs are arranged so that the test or calibration source is positioned between them. Thus, when a nuclear decay event produces photons, each of the PMTs will detect about half of them. If these photons are produced from the same decay event within the source, it is likely that they will occur in each detector within about 20 ns of each other. The electronic circuitry of the detectors is established such that only those events that yield counts in each PMT within 20 ns are recorded are recorded as valid counts. This is the coincidence function of the LSC instrument. The calibration of liquid scintillation counting detectors is given in ASTM E181. In this energy range, the efficiency of producing a photon in the cocktail is poor because of two reasons: an inability to exceed the necessary quantum threshold and pulse-summation effects. Thus, the overall efficiency of detection in an unquenched sample approaches about 65 percent for ^{3}H and 94 percent for ^{14}C.

15.5.3.1   Detector Requirements and Characteristics

For measurements in which data are expressed relative to a defined standard, the individual correction factors cancel whenever sample composition, sample mass, 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 dissolved in an appropriate solvent that achieves a uniform dispersion (this combination is commonly referred to as the "cocktail"). A second organic phosphor often is included in the liquid scintillation cocktail as a wavelength shifter. The sample then is added to this cocktail to form the test source. The beta particles interact with the solvent and primary phosphor to produce photons. The wavelength shifter efficiently absorbs the photons of the primary phosphor and re-emits them at a longer wavelength more compatible with the photo-multiplier tube. Most liquid-scintillation counting systems use two photomultiplier tubes in coincidence. The coincidence counting arrangement minimizes spurious noise pulses that occur in a single photomultiplier tube and thus provides lower background. The requirement that both photomultiplier tubes respond to each event has a slight affect on the overall detection efficiency of $E_{\beta max}$>200 keV; however, system response to $E_{\beta max}$<200 keV will be significant.

Another approach to LSC without the use of organic phosphors is Cerenkov counting. When a high-velocity charged particle passes through an optically transparent dielectric medium whose

index of refraction is greater than one, excess radiation is released in the ultraviolet range of energies. This is known as "Cerenkov radiation" (Kessler, 1986). In order to produce Cerenkov radiation, the condition $\beta \cdot n > 1$ must be met; where n is the refractive index of the medium and β is the ratio of the particle velocity in the medium to light velocity in a vacuum (Knoll, 1979). Wavelength 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 may be eliminated.

The assessment of the effectiveness of the overall system detection is based on the figure of merit (FOM) concept. This is a numerical value that is used to describe the entire counting system (cocktail plus detector). The FOM generally is obtained by the following formula:

$$FOM = \frac{(\text{Efficiency of the sample detection})^2}{\text{Detector blank background}}$$

Thus, the larger the FOM, the lower will be the limit of detection. A lower blank background, a more efficient cocktail, or a better photon detection system can achieve a larger FOM.

OPERATING VOLTAGE

The voltage of the detector is established based on the characteristics of the PMT. This is usually about 1,000 volts DC. The voltage of the PMT should not be changed because this would affect the overall quantum yield of photoelectrons produced by the decay event. Generally the voltage is a fixed parameter by the instrument manufacturer and not adjustable by the user.

SHIELDING

Most liquid scintillation units come with the sample chamber enclosed within the instrument. The manufacturers have provided a mechanism (usually a source "elevator") by which the source is moved into a shielded position (chamber) between the two PMTs. No additional shielding is usually required for LSC instruments. However, building location and room materials of construction can affect the overall background that the LSC instrument experiences. Instruments are constructed with standard shielding materials to account for routine background radiation. The potential for other than routine background radiation should be assessed prior to selecting a location for the instrument. Shielding from UV-visible radiation is discussed under the section on dark adaptation.

BACKGROUND

There are several different sources of background radiation that could affect liquid scintillation analysis:

- Building construction materials;
- Reagents used in analysis (this is the blank and is usually assessed separately from background" radiation);
- Scintillation vials;
- Presence of an energy source (reactor or accelerator);
- Presence of other radionuclides that have beta or gamma emissions that are contaminating the sample or test source under analysis;
- Stray light into the instrument; and
- Scintillation cocktail (this is the blank and is usually assessed separately from background radiation).

Although there is some capability to differentiate certain beta-particle energies, there is a wide overlap in beta particle spectra. Thus, background counts that take into account the process—as well as the instrument, reagents, and scintillation vials—should be performed routinely. Routine monitoring of background is significantly different for LSC with respect to other detection methods because the cocktail is the primary detector. For example, any component of the sample (chemical or physical) that can affect the cocktail and is not reproduced in the background test-source measurement can introduce additional uncertainty. Controls should be in place to identify and correct variations in background measurements. Variations of background and background quench also should be monitored for potential impact on results.

Another way to help achieve low backgrounds is to use scintillation-grade organic phosphors and solvents prepared from materials containing low concentrations of ^{14}C, such as petroleum. The counting vials may be made of low-potassium glass or plastic to minimize counts because of ^{40}K. Liquid scintillation provides a fixed geometry from a given size counting vial and liquid volume.

DARK ADAPTATION

The photomultiplier tubes are sensitive to any light which they detect. Stray room light will cause a signal leading to a higher background. The instruments are constructed so that they are light tight, and interior surfaces are generally black to prevent light transmission by these surfaces from stray light.

Chemiluminescence, the production of light by a chemical reaction with a molecule, can be troublesome in liquid scintillation counting. However, the duration of chemiluminescence is generally short, and waiting a few minutes after mixing the reagents will allow the effect to dissipate before counting starts. Phosphorescence, the emission of light caused by photon interaction with a molecule, will cease a short time after being placed in the dark. This is referred to as being "dark adapted" (Faires and Boswell, 1981).

The two factors which can produce the phosphorescent effect on the cocktail are external UV light and heat. Each of these work by a similar mechanism. Energy is transferred to the fluor

(either by UV excitation or heat) and the fluor excites/de-excites yielding photons in the detection range of the PMT. These events can contribute to the total background and increase the detection limit of the analysis or could lead to falsely elevated sample results. Interference from UV light from lamps or the sun is avoided by dark adapting the source in the LSC vial for at least 30 minutes prior to analysis. To avoid differences in background because of thermal excitation, most instruments have internal thermostats to maintain constant temperature during the analysis. These instrument characteristics allow sufficient time for phosphorescent and luminescent states, unrelated to the radioactivity measurement, to undergo de-excitation prior to counting the source.

CHANNEL OVERLAP

The traditional concept of "channel" for liquid scintillation was an energy range that corresponded to the majority of the energy distribution of a particular radionuclide's beta particle distribution. Counting in "channel 1" indicated tritium, or "channel 2" indicated ^{14}C. The size of the channel was determined by setting discriminator levels. The amount of quench in a test source would cause a spillover of the higher energy distribution beta particles to the lower channels. Also, the high energy distribution of a lower energy beta could cross into the higher energy beta channel. This was referred to as "channel overlap." In older instruments, the sample-channel-ratio method was used to separate the components. Recent advances in liquid scintillation instruments have made it easier to eliminate or account for this overlap. Similar to gamma spectrometers, liquid scintillation units now divide the energy output of the PMT into more discrete channels (usually about 1,000). Mathematical modeling of the spectrum shape based on these discrete channels allows more refined techniques to be used to account for channel overlap.

15.5.3.2   Calibration- and Test-Source Preparation

Gaseous radionuclides most often measured include tritium, both as a vapor (^{3}HOH) and in the elemental form (^{3}H-H), ^{14}CO$_2$, and the noble gases, ^{37}Ar, ^{41}Ar, ^{85}Kr, ^{222}Rn, ^{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 bath at sub-zero temperatures. A measured aliquant of the collected water is analyzed by liquid scintillation spectrometry (EPA, 1984b). Tritiated water vapor sometimes is collected by pulling air through a trap containing materials like silica gel (SC&A, 1994) or through a molecular sieve. 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). For this method, it is very important to de-aerate the liquid prior to introducing the gas since gaseous components may cause quench. The temperature should be carefully controlled since gas solubilities are generally inversely proportional to the temperature (NCRP, 1978).

Tritium is the radionuclide most often measured by liquid scintillation counting (DOE, 1997; EPA 1979; Lieberman and Moghissi, 1970). 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 cocktail 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, for example, *n*-hexane or cyclohexane (Moghissi, 1981; EPA, 1979). An aliquant of the collected water 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 mass difference (three times) between ^1H and ^3H (DOE, 1997; EPA, 1984a). Tritium becomes enriched in the liquid phase 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).

Environmental and biological samples also can be analyzed for total ^3H (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 ^3H 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 ^3H 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.

15.5.3.3   Detector 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 test-source medium.

Except for test sources with very predictable amounts of quenching, it is necessary to determine a counting efficiency for each laboratory test source. 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 the 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 then can be determined from the spiked aliquant and applied to the unspiked aliquant (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 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. A quench curve is then prepared by plotting a parameter obtained from the external standard spectrum against counting efficiency (Kessler, 1989).

QUENCH

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: chemical or color quenching. Color quenching results in a reduction of the scintillation intensity (as seen by the PMTs) because of absorption of the fluor scintillation by colored materials present in the cocktail. Thus, a reduction in counting efficiency occurs after the particle energy has been transferred to the fluor. Chemical quenching results in a reduction in the scintillation intensity because of the presence of materials in the scintillation solution that interfere with the process energy transfer to the fluor also leading to a reduction in counting efficiency. Chemical quenching results in a reduction in the scintillation intensity because of 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. Suspended solids and opaque materials also will cause quench in the cocktail, because they physically obstruct the light path to the PMTs.

One can have all three types of quenching present in a test source. Although the mechanisms of chemical and color quenching may be different, they both affect the number of photons reaching

the detector. Therefore, the measured sample counts should be corrected for quenching effects so that the radioactivity in the test source can be quantified. Some of the stronger chemical quenching agents are alkyl bromides, iodides, nitrates, mercaptans, and ketones (NCRP, 1978). Yellow provides the most significant quench.

The quantitative measure of quench can be seen in the beta particle spectrum of the quenched *versus* unquenched test source. Not only does quench reduce the total number of photon events received by the detectors, but it also shifts the distribution of the events to lower energy. This causes the $E_{\beta max}$, as well as the other mathematical characteristics of the beta curve, to shift to lower energies.

Quench may play an important role in the analysis for surface contamination levels of low-energy beta-only emitters, such as ^3H, ^{14}C, ^{63}Ni, ^{135}Cs, etc. As discussed in Section 10.6, swipes are used for assessing gross surface contamination levels. Thus, chemical separations or sample cleanups are not usually performed, and the entire swipe will be inserted into the scintillation vial. Several different parameters affecting quench will also affect determining the consistency of the results if direct analysis of the swipe is used. Some of these factors are:

- Material from the surface analyzed which dissolves in the cocktail yielding either a chemical or color quench;

- Insoluble detritus that can become suspended in the cocktail, interfering with the emitted fluor radiation reaching the PMT;

- Adhesives or adsorbent materials used in the swipe material itself may react with the fluor, or may interfere with the transfer of energy to the fluor; and

- The degree of transparency of the swipe material to the counting system (i.e., the photons emitted by the fluor may be absorbed by the swipe material).

When this type of analysis is being performed, either a dry or wet swipe could be used. However, the analyst should ensure that the conditions cited above are accounted for by performing a test of the particular swipe and the surface type to assess their affect on quench.

COMPENSATION FOR QUENCH

Most liquid scintillation spectrometers manufactured after about 1965 have a method of assessing the quench level in a solution compared to the standard, allowing for correction of the quench. Historically, quench was accounted for by establishing a quench curve for the instrument or by using standard additions. A quench curve is made by taking a standard and analyzing several replicates under conditions of varying amounts of added "quench" agent. Typically, any strong color agent could be used as the quench.
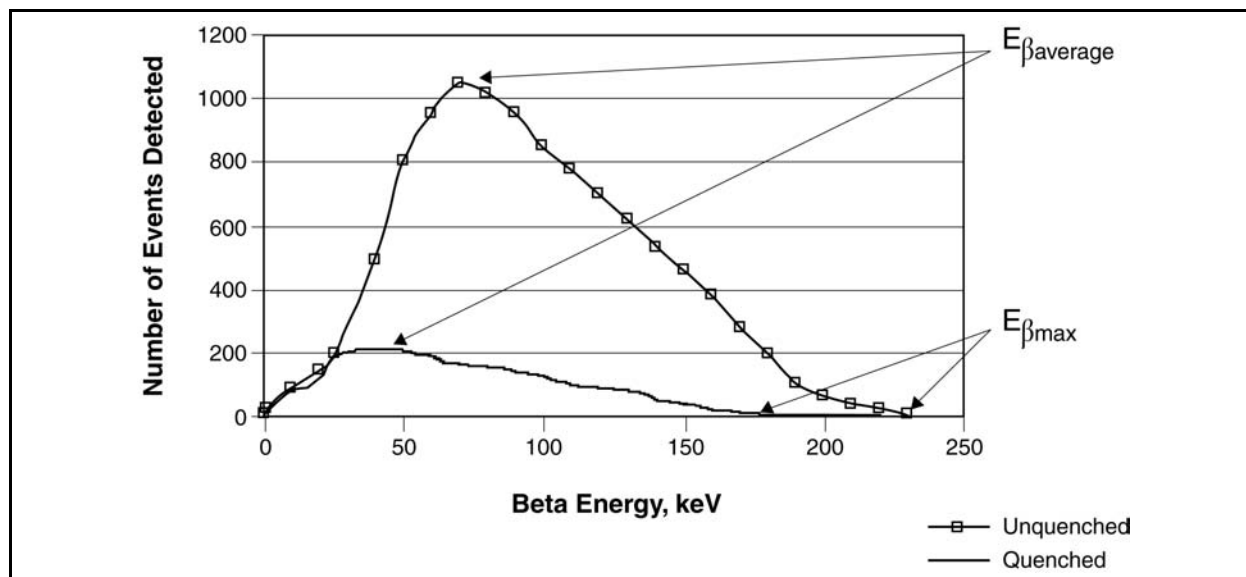
FIGURE 15.5 — Representation of a beta emitter energy spectrum

Figure 15.5 shows the effect that quench would have on the beta spectrum. Note first that the average beta energy is shifted to a lower energy. Second, the total number of events at each energy is lower than the unquenched source.

Historical quench corrections include channels ratio, external standard, and internal standardization. More recent methods are the H-number and tSIE methods. One of the methods used to assess the quench is the H-Number technique (Horrocks, 1970). Fundamentally, the beta-particle spectrum generated in the cocktail by a standard external gamma source (^{137}Cs) is analyzed over the energy range of the instrument. Each energy interval receives a number of counts corresponding to the generated Compton events (these are significantly greater than the test-source output pulses because of the gamma intensity). The inflection point of the beta curve at the high end of the energy distribution is assigned a channel number for that solution with no added quench. Increasing levels of quench shifts this inflection point to lower channel numbers. The quench is a measure of the change in the channel number of the inflection point compared to the unquenched solution.

Another method uses the transformed spectral index of the external (tSIE) standard (Kessler, 1989). This technique uses the energy distribution of the entire spectrum as generated by an external ^{133}Ba source when it is exposed to the cocktail. The accumulation of this energy spectrum takes a few seconds and the events produced are far greater than those of the test source because of the intensity of the ^{133}Ba source. The effects of the radioactivity in the sample are independent of this measurement.

The manner in which quench affects the electron distribution produced by the external source

will be the same for standards and samples, since quench is the interference of energy transfer. With environmental samples, the degree of quench for all practical purposes is independent of the material that causes the quench ("quench is quench," regardless of the cause).

The fluors used in cocktails are susceptible to excitation by both light (artificial room light or sunlight) and heat. Furthermore, these materials also will have phosphorescent states, which can have significant lifetimes (minutes). It is important to ensure that the standards for quench-curve preparation and the sample are "dark adapted" for the same period of time prior to their analysis. This allows all of the phosphorescent states to de-excite and not add to the measured counts, and helps to ensure that the interference form other sources of excitation are minimized.

The level of quench affects the measurement uncertainty of the analysis in two ways. First, it decreases the net count rate of the test source. Since the relative measurement uncertainty is directly proportional to the square root of the counts, the relative uncertainty increases. This uncertainty can be directly quantified. Second, the measure of quench itself is not exact and will be characterized by a Gaussian distribution at a specific quench for a specific test source. Additionally, the quench function is generally exponential. This means that the determination of quench in an individual test source is made from a smoothed curve. Unless a specific effort is made to assess this uncertainty component, it is not accounted for in most software analysis of the final calculation. Minimizing the quench will minimize the increase in the combined standard uncertainty of the measurement.

Beta particles, unlike alpha and gamma rays, are emitted in a continuum up to an $E_{\hat{a}max}$ (Figure 15.5). The continuum covers a wide range of energies, so that different beta-emitting radioisotopes having different energies may have overlapping energy continua. The average beta particle energy is roughly one-third of the $E_{\hat{a}max}$. This energy generally has the highest population of all the beta particle energies emitted by that particular radionuclide. As an example ^{90}Sr has an $E_{\hat{a}max}$ of 546 keV and ^{89}Sr has an $E_{\hat{a}max}$ of 1,490 keV. Their beta-particle spectra overlap significantly. They cannot be separated chemically. Neither of these two isotopes is a strong gamma emitter. Thus, the analysis of these two beta emitters sometimes is performed indirectly, using liquid scintillation, by using the ingrowth of ^{90}Y and mathematically solving for the initial concentrations of ^{89}Sr and ^{90}Sr.

A liquid scintillation spectrometer detects beta-particle events as a result of beta energy transfer into a liquid medium, which promotes the formation of photons in the UV/visible energy region. The transfer is an indirect process. The beta particle distributes its energy through solvent "excimers" to an organic fluor, which de-excites by releasing the UV/visible photons. Any component of the cocktail that affects the energy transfer process will have a significant effect on the analysis. Other controllable aspects of the cocktail are:

- The ratio of the sample volume to solvent-to-fluor volume;
- Preparation of the quench curve;

- Stability of the cocktail; and
- Dark adaption of the cocktail.

Each analytical procedure for scintillation analysis should find the sample-to-fluor volume that provides the maximum response. Part of this process is that the analyst is ensuring that sufficient fluor exists to convert the beta particles to UV/visible region photons (i.e., scintillator capacity). Once this ratio is established, a quench curve is made using the same ratio of sample-to-fluor solution.

The most significant aspect of liquid scintillation analysis is accounting for quench in the sample and standards to the same extent (or by an equivalent methodology), so that the analytical results are reproducible and accurate.

Beta and alpha particles both will induce a fluorescent spectrum in the liquid scintillation cocktail. The beta spectra originate at zero energy and cover a large range of energies. The alpha-particle distribution is much different, in part because of the discrete energy distribution. Although the liquid scintillation process has transformed the original energy of the beta particles to a measurable quantity on this spectrometer, the distribution of the actual beta-particle energies is exactly the same as the distribution of the UV light detected by the spectrometer. It is difficult to distinguish one beta emitter from another for this reason of continuous beta-particle energy, unless the beta-particle energies are very different. Alpha analysis using liquid scintillation is less complicated because of the distinct energy emitted by the alpha particles. The signal from the alpha particles can be distinguished from that of the beta because of the delay time for the fluor excited state to decay. Because alphas have such a significant energy directly imparted to the fluor, a triplet state of the excited electron is achieved.

This state must first decay to the singlet electron state before fluorescence can occur, as in beta interactions. The Δt for this process is about 35 ns, so it can be segregated electronically from any beta signal. The problems of quench will occur in alpha as in beta spectroscopy, since quench occurs not with the actual radioactive decay mode, but with the energy transfer from the fluor to the detector. Refer to section 15.4.5 ("Photon Electron Rejecting Alpha Liquid Scintillation") for details about a method of performing alpha analysis in liquid scintillation media.

COCKTAIL

The liquid scintillation cocktail is the combination of the scintillator (primary and secondary) and solvent. The combination of the cocktail with radionuclide solutions is referred to as the "test source" or "calibration source." The scintillators are organic materials which over time can undergo decomposition. As with other organic compounds of this type, they are light and heat sensitive. Thus, it is important to protect them from light and heat to minimize their degradation during laboratory storage.

The test source also will be susceptible to degradation because of changes in temperature and addition of chemicals from the sample. It is therefore important to know how much sample to add to the fluor solution and how long it can be stored without degradation.

The ratio of fluor solution to sample (which comprises the cocktail) should be optimized for each radionuclide and sample type analyzed. This can be done by first selecting a final volume of the cocktail that will fill a vial to 80-90 percent of its volume. Then, make several combinations by varying the ratio of a standard radionuclide to the fluor solution so that the final volume is constant. Count all the vials for the same time period and find the ratio that achieves the highest relative count rate.

15.5.3.4   Troubleshooting

There are many areas involving the processing of a sample by liquid scintillation analysis where errors can be introduced. Identified here are some of the more common problems that have been experienced with suggestions on how to correct them:

- Routine background check is above upper control limit on QC charts
  - Insufficient dark-adapt time
  - Light leak has developed into the instrument
  - Contamination of the fluor solution with a radionuclide calibration solution
- Routine QC check of test source (using a flame-sealed, unquenched source) is below lower control limit
  - Wrong channel or range selected
  - Smudges on scintillation vial
  - Decay correction not used or improperly applied
- Test-source count rate appears to change during count interval
  - Cocktail separation has occurred during the count interval
  - Background has changed during the count interval
  - Insufficient dark adapt period
  - Temperature change of instrument
- Instrument check with unquenched source yields low readings
  - Source not fully inserted into instrument
  - Decay correction not used or improperly applied
- Test-source or QC count rate is unusually high
  - Contamination in cocktail from another radionuclide or higher concentration
  - Insufficient dark adaptation

15.6 Gamma Detection Methods

This section describes the measurement of gamma-ray activity. Since gamma radiation is a

penetrating form of radiation, it can be used for nondestructive measurements of samples of any form and geometry as long as calibration sources of the same form and geometry are available. Radionuclides separation followed by sample digestion can be used to improve the detection capability of gamma-ray-remitting analytes by concentrating the analyte and reducing interferences. Attenuation of gamma radiation is generally small, but because of variations in sample density, sample thickness, container shape, or container thickness, it must be corrected either by using calibration sources that match the sample/container densities and containers or by appropriate mathematical formulas (Modupe et al., 1993; Venkataraman et al., 1999):

Photons interact with matter in one of three ways:

- Photoelectric effect, where all energy is transferred to an electron in the absorber matrix;
- Compton scattering, where an electron in the absorber matrix is scattered and only part of the initial photon energy is transferred to that electron; and
- Pair production, where the photon energy is converted to positron-electron pair in the vicinity of a nucleus.

For the photoelectric effect, the entire gamma energy is transformed into a detector pulse, eventually resulting in the full-energy peak (FEP) observed in the gamma spectrum. The Compton scattering effect is seen as continuous, broad band radiation (referred to as the "Compton continuum"), which terminates at the Compton edge. This is a distinct decrease in the recorded counts in the continuum. This edge occurs between 150 and 250 keV below the FEP. The remainder of the energy is carried away by the scattered gamma ray. Pair production requires a minimum gamma ray energy of 1,022 keV, since the sum of the rest masses of a positron-electron pair is this amount.

The energy of the gamma ray in the pair production effect is split between the formation of the positron and electron. The positron is a very short-lived particle and annihilates an electron in the absorber matrix. This annihilation process creates two 511 keV photons. These may or may not be detected by the detector. The energy spectrum recorded from this event may have five distinct peaks that appear to be gamma rays: the FEP (1,275 keV), a single escape peak (FEP-511 at 765 keV), a double escape peak (FEP-1,022 at 254 keV), a 511 keV peak, and a sum peak (FEP+511 at 1,786 keV). Figure 15.8 (page 15-80) shows some of these additional peaks.

The extent to which each of these effects is seen depends upon the gamma ray energy, the sample matrix, and the detector material. The mass attenuation coefficient is a measure of the probability that a gamma ray will interact with the absorbing medium. Figure 15.6 shows the relative mass attenuation coefficients of each of the three predominant photon interactions with high-purity germanium.

Since different radionuclides emit distinct and discrete spectra of gamma radiation, the use of an energy discriminating system provides identification and quantification of all the components
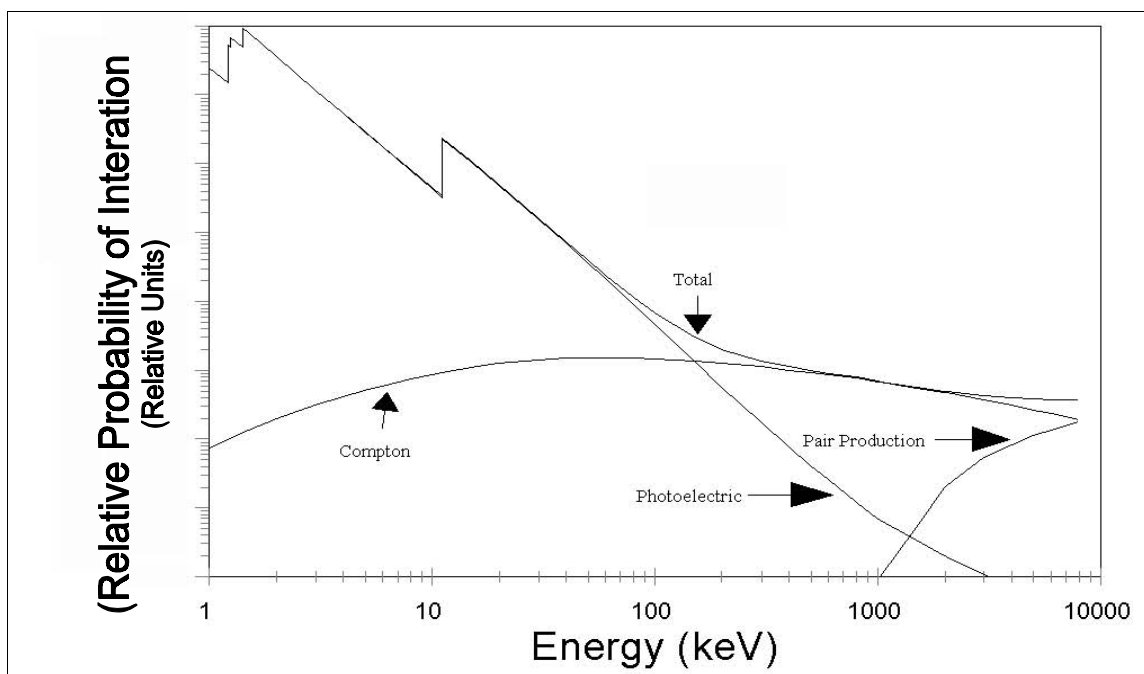
FIGURE 15.6 — Gamma-ray interactions with high-purity germanium

present in a mixture of radionuclides. General information on gamma-ray detectors and gamma counting is covered in the literature (Friedlander et al., 1981; ICRU, 1992; Knoll, 1989). 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. The more commonly used solid detectors are discussed in this section.

15.6.1 Sample Preparation Techniques

Important considerations in preparing calibration sources for gamma-ray spectrometry are geometry (shape), size, and homogeneity (uniformity) of the source. Calibration sources can be in any reproducible shape or size, but the radionuclides need to be uniformly distributed throughout. A counting container that allows the source to surround the detector, thus maximizing the geometrical efficiency, is referred to as a "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.

Two important advantages of gamma-ray spectrometry are the ability to measure more than one radionuclide simultaneously and the elimination or reduction of sample dissolution and radionuclide separations (i.e., gamma-ray spectrometry can be a nondestructive sample analysis).

15.6.1.1   Containers

Source configurations for nondestructive analyses generally are selected to optimize counting efficiency for the particular sample type and its expected activity. This also means that the containers are selected to minimize attenuation of the particular gamma rays, and to have sufficient integrity to keep the sample intact. For quantitative analysis, the calibration and test sources (samples) are counted in the same type of container. Different types of containers might be used for qualitative analyses.

15.6.1.2   Gases

Sample containers for gasses will generally have a provision so that the container may either be evacuated (using a vacuum pump) or purged (having sufficient sample so that the container may be flushed with approximately 10 sample volumes). This is generally accomplished using inlet and outlet isolation valves. These may be constructed of either plastic, stainless steel, or glass. These containers are then brought to atmospheric pressure, which minimizes losses because of pressure differential, during storage, transport and counting. Analysis at pressures other than atmospheric may be made, however, a correction using the ideal gas laws needs to be made.

Sample containers for gaseous or atmospheric samples may use concentration devices to enhance the detection limits for certain radionuclides. A concentrated sample matrix, such as a solid, represents the aerosol collected. The detector calibration needs to be performed with a matrix and source container that matches the test source and container. Examples of this are:

• Charcoal canisters (aluminum cans that contain inlet and outlet retention elements and are filled with charcoal and may be impregnated with potassium iodide, KI or triethylene diamine [TEDA]), used for iodine or noble gas collection.

• Molecular species filtering (EPA, 1990) that 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.

• Zeolite canisters (aluminum cans that contain inlet and outlet retention elements and are filled with silver-alumino-silicate materials) for iodine collection.

In each of these cases the distribution of the radionuclide on the medium most likely will not be uniform. This is especially true for the filled canisters where the flow inlet end will have a significantly higher loading than the outlet, unless the medium has gone to saturation. The positioning of the sample container on the detector in a reproducible geometry to that of the standard becomes very important for these types of samples.

15.6.1.3   Liquids

Containers normally used for liquid analysis are:

• Marinelli beakers of 0.25 to 4 L to measure liquid sources (water, milk, and food samples blended to a uniform slurry);
• Plastic bottles of standard sizes such as 250, 500, or 1,000 mL; or
• Scintillation size vials (20 mL) for samples of more significant activity.

If greater counting efficiency is required, the 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 coprecipitating the desired radionuclides and collecting them on filter paper; and
• Concentrating the radionuclide on a resin.

It should be noted that the final sample configuration should not only be homogeneous, but should also match the geometry of the standard used to calibrate the detector.

A radionuclide in solution may be purified by chemical techniques (i.e., impurities removed), after which 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 (Blanchard et al., 1957). For the analysis of test sources having significant solids containing low-energy gamma emitters, absorption curves can be prepared. Solid samples may need to be air-equilibrated prior to counting to ensure that a consistent moisture film is present, which is accounted for by self-absorption measurements in standards and samples.

In the case of all dry sources, steps should be taken to prevent solids from exiting the test-source mount or container, which will affect the measurement and, in time, contaminate the detector.

15.6.1.4   Solids

A variety of containers are used for solids analysis such as:

• Cylindrical plastic containers of various volumes, such as the 400 mL "cottage-cheese container," and Marinelli containers;
• Planchets and plastic culture dishes of various diameters to measure precipitates, air filters, etc.;

- Aluminum cans (like the "tuna can" configuration) of a standardized volume into which solid sources can be compressed, and sealed, if desired, to retain volatile materials; and
- 47 mm (2 inch) diameter, 0.45 μm pore size particulate filters, which are enclosed in a petri-style dish after sample collection.

Sometimes, other samples may be reduced in volume by:

- 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 digestion or ashing, if volatile radionuclides are not of interest.

Many of the sizes of these containers have been retained for historical consistency (PHS, 1967a).

Solid samples analyzed directly by gamma-ray spectrometry do not need to be dried prior to analysis as do samples for alpha or beta counting. However, it is important that the sample and standard geometries match, and that the sample water content should be known so that dry-weight concentration can be calculated.

15.6.2 Sodium Iodide Detector

Sodium iodide has a high density, which makes it an attractive solid material for detecting high-energy gamma radiation. The crystal is activated with 0.1–0.2 percent thallium to improve its scintillation characteristics in the visible range. In scintillators such as NaI(Tl), the gammas interact by excitation of electrons in the valence (or bound) states of the atoms to an excited state called the conduction band. Energy is released as light (visible and UV) photons when the electrons return to the valence band. These scintillations are easily detected and amplified into useable electrical pulses by a photomultiplier tube. The NaI(Tl) detector is the recommended detector for gross-gamma or single-radionuclide counting because of its high efficiency and room temperature operation.

15.6.2.1 Detector Requirements and Characteristics

The sodium iodide crystal usually is sealed in an aluminum enclosure called a "can." The crystal is hygroscopic and sensitive to shock and fracture. The geometry of the detector "can" may be flat or well shaped, but numerous shapes have been made for specific applications. One of the most common sizes for the detectors is the 7.5×7.5 cm (3×3 inch), but they can come in many sizes, including some specially constructed to contain several hundred pounds of the scintillator. The well-shaped detectors are of higher efficiency for the same volume of detector. This particular characteristic allows almost a 100 percent efficiency (so-called 4π geometry) for low-energy gamma-emitting test sources that can fit inside the well.

A gamma energy of 300 eV will release about ten light photons when it interacts with the crystal. This is the minimum energy necessary to create a photoelectron at the first dynode of the PMT. The PMT is optically coupled to the base of the NaI(Tl) detector to minimize any loss of photons, and maximizing efficiency. The size of the final voltage pulse (referred to as the "pulse height") received from the PMT is directly related to the energy of the gamma which interacted with the sodium iodide crystal. Electronic circuitry connected to the PMT output can perform pulse-height-analysis (PHA). This is merely counting the number of events with a certain pulse height. The output of the PHA can then be stored using a multichannel analyzer (MCA which is subsequently displayed on a screen), or summed over a specified energy range (this device usually referred to as a "scaler" or a "single channel analyzer," SCA).

The following components complete the NaI(Tl) gamma-ray spectrometry system:

- HIGH-VOLTAGE POWER SUPPLY. 1,000 to 3,000 volts DC regulated to 0.1 percent with a ripple of not more than 0.01 percent.

- PRE-AMPLIFIER/AMPLIFIER. The combination shapes and linearly amplifies the PMT output to a maximum of 10 volts.

- MULTI-CHANNEL ANALYZER (MCA). The amplifier output is directed to the PHA. The PHA will sort the individual events and send them to discrete energy registers so that a count vs. energy graph can be displayed. The system usually has a low energy cut off to eliminate low energy background signals which will increase MCA processing time.

- SINGLE CHANNEL ANALYZER (SCA). A single-channel discrimination system is set with a lower and upper level discriminator (LLD and ULD). The lower limit is usually referred to as the "threshold" and the difference between the two limits is the "window." Only those pulses from the amplifier within the window will be sent to the scaler. Any pulses lying outside the preset limits are rejected. The scaler takes the sum of all counts within the window for a pre-set time. The SCA application of a NaI(Tl) detector commonly is used to analyze gamma-ray emitters (such as ^{85}Sr) when they are used to monitor chemical yield.

- BETA ABSORBER. A beta absorber of 3–6 mm of aluminum, beryllium, or poly(methyl methacrylate) should completely cover the upper face of the detector to prevent betas from reaching the detector.

Figure 15.7 is a gamma-ray spectrum of ^{137}Cs collected using a NaI(Tl) detector. The features of note in this spectrum are:

- The FEP at 661 keV;
- The Compton edge at about 470 keV;
- The backscatter peak from the detector shielding at about 215 keV;

- A broad peak at about 35–40 keV as a result of the photoelectric absorption of the 37.4 keV barium K-shell X-ray (from the Cs decay) and the 35 keV iodine K-shell X-ray (from the iodine in the detector); and
- The FWHM of about 53 keV.

One characteristic of a detector which helps to define its utility is the peak-to-Compton ratio. This is the number of maximum counts in the peak centroid channel of the FEP divided by the average number of counts in the Compton edge (ANSI/IEEE 325). For example, the peak-to-Compton ratio for ^{137}Cs would be the maximum counts in the 661 keV peak (assumed to be the peak centroid channel) divided by the mean counts per channel between the 440 and 490 keV Compton region. In Figure 15.7, this value is about 9.

Another characteristic is the FWHM of the detector. FWHM is the width of the peak at one half of the counts in the peak centroid. This characteristic is based on the range of energy levels available for the electrons to de-excite from after they have been promoted into the conduction band. Because the NaI(Tl) operates at room temperature this represents a broad range of energies. The value for the 661 keV peak here is about 53 keV. The FWHM varies slightly as a function of gamma ray energy for a NaI(Tl) detector.

A low-energy peak around 35 keV may be present as a result of the gamma-ray interaction with an iodine K-shell electron through the photoelectric effect. When the K-shell is filled by the
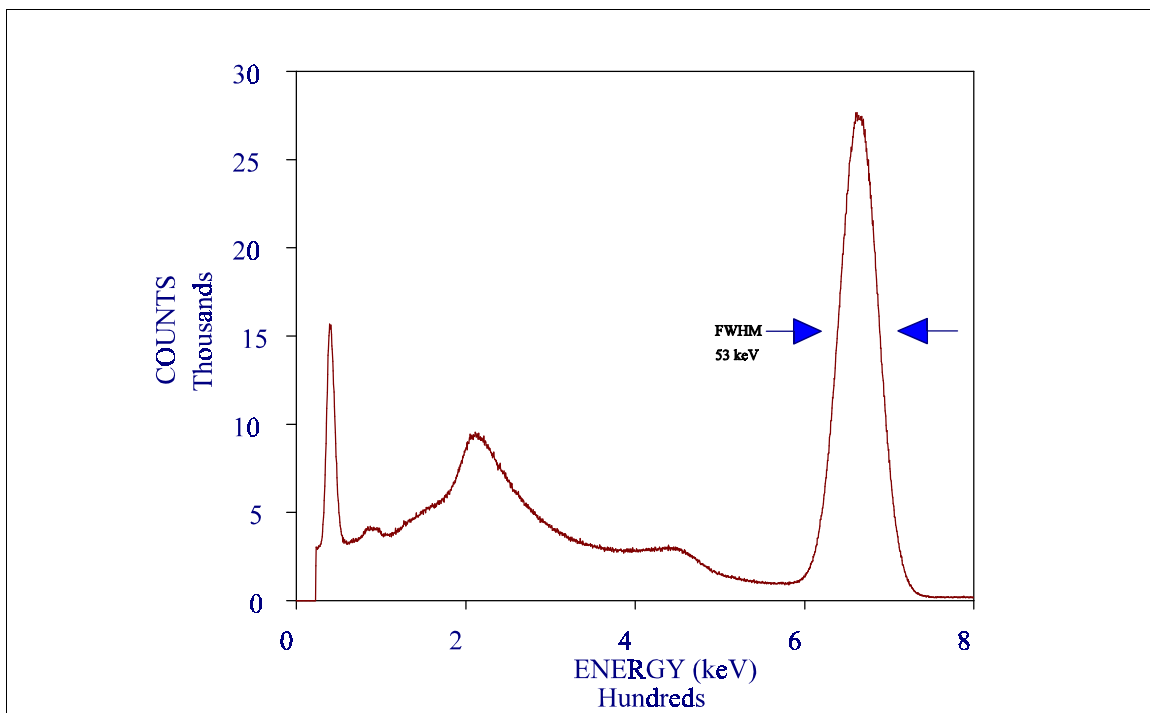
FIGURE 15.7 — NaI(Tl) spectrum of ^{137}Cs

Auger effect, the resultant release of 28 keV may be delayed enough from the original electron signal to be detected as a separate event. An additional feature (not discernable in this spectrum) is a small peak 28 keV less than the FEP, which is referred to as the "iodine escape peak." This effect is most prominent with gamma ray energies less than 150 keV. Superimposed on the low energy peak is also the X-ray emission from the decay of cesium.

Finally, the wide band at about 215 keV results from gamma rays emitted from the sample interacting with the detector shielding (usually lead) through the Compton effect. The Compton effect radiation is backscattered from the shielding to the detector. For gamma radiation in the range of 600–3,000 keV this backscatter area is from 180 to about 250 keV.

15.6.2.2   Operating Voltage

The crystal itself does not have a voltage applied to it. The voltage requirement is for the PMT. This depends on the manufacturer of the PMT, and ranges from 1,000–3,000 V DC. The remainder of the components of the system can be fed off of a 120 V AC power source. The power supply to the entire spectrometer should be on a filtered and regulated line.

15.6.2.3   Shielding

For most applications, NaI(Tl) detectors are shielded to reduce the X-ray and gamma-ray background from nonsample sources. However, the amount and type of shielding will depend on the particular application. For low-level environmental sample analyses, a typical arrangement is about a 13-cm thick lead shield (rectangular or cylindrical configuration) with its inner surfaces lined with cadmium then copper (or a thick copper sheet) to reduce lead X-rays and backscatter photons originating from the shield walls.

15.6.2.4   Background

Detectors have a certain background counting rate from naturally occurring radionuclides and cosmic radiation from the surroundings and from the radioactivity in the NaI(Tl) itself. The background counting rate will depend on the amounts of these types of radiation and on the sensitivity of the detector to the radiations. The most significant source of background for the sodium iodide detection system is the PMT. Thermionic noise is the spontaneous emission of electrons from the photocathode in the PMT, leading to a final pulse. This noise results in a background rate of about 50 cpm per cm^3 of crystal over the entire energy range. However this value is specific for each PMT used and may increase with PMT age.

Another contribution to the background can come from the PMT material itself. For low level counting applications, a quartz PMT rather than an ordinary glass PMT will yield lower count rates because of reduced levels of ^{40}K and ^{232}Th.

Shielding can also be a source of background radiation. Old lead should be used, since the contribution from naturally occurring ^{210}Pb (t$_{1/2}$ ≈ 22 y) and its progeny will lead to *bremsstrahlung* radiation from beta decay in the energy range <100 keV. Steel processed after World War II may contain small quantities of ^{60}Co.

15.6.2.5   Detector Calibration

Standards used for calibration of the NaI(Tl) detector should allow all of the photopeaks to be analyzed within a reasonable period of time (i.e., hours) and achieve less than 1 percent counting uncertainty (for the net peak area) in each photopeak used for calibration.

For a NaI(Tl) detector, the energy calibration should be checked on a periodic basis (weekly to monthly), using individual source energy standards (generally one radionuclide per source with only 2-5 gamma rays). This ensures that the individual gamma ray can be seen because of the wide energy resolution of the NaI(Tl) detector. The plot of gamma ray energy vs. channel number should yield a linear graph over the energy range used.

15.6.2.6   Troubleshooting

The three parameters that routinely should be checked and recorded are:

• Energy calibration (keV/channel),
• Counting efficiency (count rate/emission rate), and
• Gamma-ray peak resolution (FWHM).

With the exception of a complete detector or electronic component failure (no pulses are detected at the amplifier or PMT output), degradation of gamma-ray peak resolution will be the first indication that a detector is not performing properly or that electronic noise has been introduced into the counting system by electronic components, such as the pre-amplifier, amplifier, or MCA. Any indications that the detector efficiency is not within statistical limits of expected values should be recorded, and corrective action taken, because this is the parameter used to convert the observed count rate to a test-source activity. The energy calibration either should be recorded with the sample spectral data or the amplifier gain should be adjusted daily to a previously established constant value.

Sodium iodide 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 environment of the detection system can cause high-voltage arcing, which results in poor peak resolution or complete system failure. Poorly conditioned NIM power can introduce electronic noise that also will result in degraded peak resolution. Positioning and routing of cables among the detector, electronics, MCA, computers, and monitors may be important when evaluating electronic noise.

A nonreproducible count rate sometimes may be traced back to degraded cable connections or cracked insulation. These problems may be caused by bending, pinching, or compression of the cable during installation, or when moving shielding for the detector.

15.6.3 High Purity Germanium

The high purity germanium detectors (HPGe) have almost completely replaced the older lithium-drifted germanium detector. HPGe detectors have less than 1×10^{10} impurity atoms per cubic centimeter of germanium. The biggest advantages of HPGe detectors is that they may be warmed to room temperature without damaging the crystal, and the energy resolution is much improved over the lithium-drifted germanium detectors. Crystal sizes of more than 200 cm^3 can be made that significantly improves their efficiency over older style detectors as well.

15.6.3.1   Detector Requirements and Characteristics

HPGe detectors are maintained within an evacuated metal container (usually aluminum) referred to as the "can." The detector crystal inside the can is in thermal contact with a metal rod called a "cold finger." The combination of metal container and cold finger is called the "cryostat." The cold finger extends past the vacuum boundary of the cryostat into a dewar flask that is filled with liquid nitrogen. The immersion of the cold finger into the liquid nitrogen maintains the HPGe crystal at a constant low temperature. This helps to ensure the reproducibility of the electronic measurement as well as reduce spurious detector events (thermionic background).

In semiconductor detectors such as high-purity germanium the gamma photons produce electron-hole pairs and the electrons are collected by an applied electrical field. Detectors may have several different configurations and the location of the sensitive region of the detector is a function of how the detector was prepared. A common configuration is the cylindrical form in which the active detection region is a concentric cylinder within the entire detector crystal. This is referred to as a coaxial configuration. Additional information on the configuration and applications of HPGe detectors may be found at www.ortec-online.com, www.pgt.com, and www.canberra.com. A charge-sensitive pre-amplifier is used to detect the charge produced in the crystal, and produce an electrical pulse suitable for direct amplification. The detector pre-amplifier usually is an integral part of the detector/cold finger assembly in order to minimize the electronic noise and signal loss because of lengths of cable.

The output pulses from the pre-amplifier 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.

Overall detector performance can be affected by count rate because 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 (positive) and N (negative) layers 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 to respond to events but the detection system may not produce reliable data. If a second (or third) event takes place while the first set of charge carriers are still in transit, the energy from the second event may not be recorded because of the detector insensitivity during the charge transfer to the electrodes. This phenomenon is known as detector "dead time." Generally the detector dead time is small compared to the ADC dead time. The ADC dead time is larger since it is processing and sorting all the signals from the detector. Another common event at high count rates is two gammas interacting with the detector simultaneously, their charge pulses getting added together, causing a sum peak. (See Section 15.6.3.3, "Troubleshooting," for a discussion of dead time problems.)

The description for electronic equipment associated with the HPGe detector is similar to the descriptions for the NaI(Tl) detector. The controls on electronic noise and voltage for each component is much more stringent for the HPGe detector.

Displayed spectra for HPGe detectors have different characteristics from the NaI(Tl) described in the previous section. HPGe efficiencies are lower for detectors equal in size to a NaI(Tl). However the energy resolution of the HPGe is much superior to that of the NaI(Tl). The energy required to cross the band gap in a germanium detector is on the order of 3 eV per event compared with 300 for NaI(Tl). Figure 15.8 shows the gamma spectrum for ^{22}Na. The FWHM of the gamma peaks here is about 2 keV, compared with the 60-70 keV for the NaI(Tl) detector. This characteristic is a function of energy and the Table 15.6 identifies how the FWHM will change for a particular detector as a function of energy.

TABLE 15.6 — Typical FWHM values as a function of energy

Energy, keV	100	600	1300
FWHM, keV	1.3	1.8	2.1

Peak-height-to-Compton ratio is another spectral parameter which is much improved for HPGe over NaI(Tl). The value for HPGe is between 30 and 50, compared to 9 for the NaI(Tl) detector.

OPERATING VOLTAGE

The germanium detector has a voltage applied directly to the crystal as opposed to the NaI(Tl) which has voltage applied to the PMT. The voltage for the HPGe is 1,000–5,000 V DC. The voltage supply unit for the detector should be on a line conditioner so that small variations in line voltage are normalized to a constant voltage. The line conditioner will also prevent power surges to the detector crystal which could destroy or severely alter its detection capabilities.
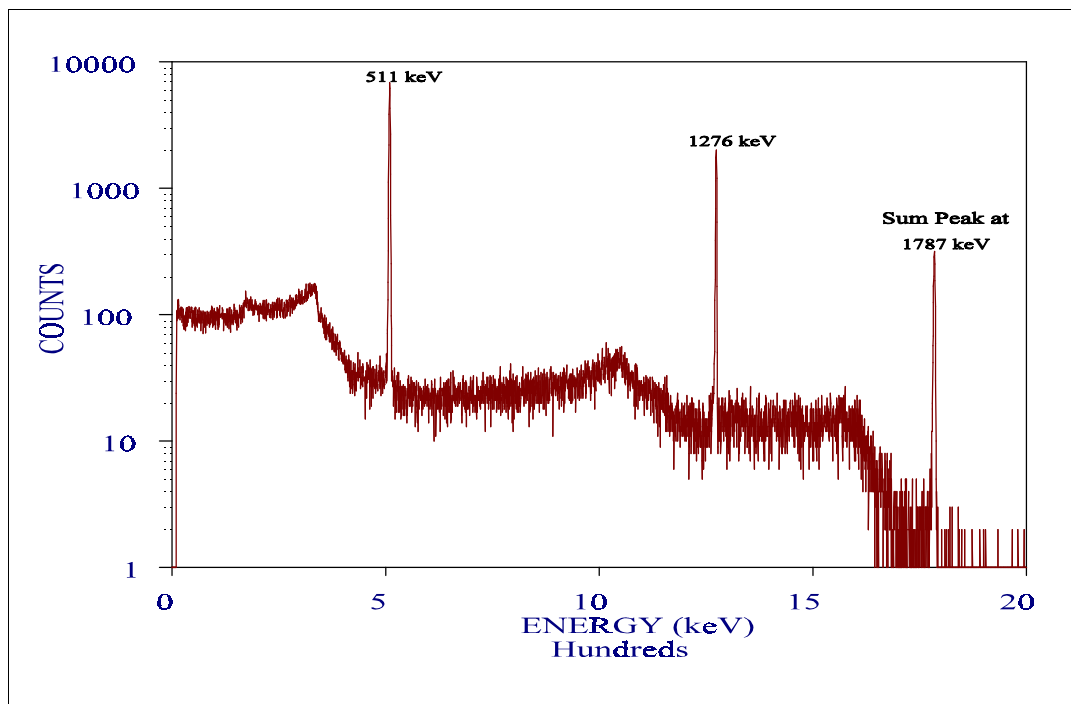
FIGURE 15.8 — Energy spectrum of ²²Na

Powering up a detector needs to be performed in a controlled manner at 50-100 volts/second to minimize shock to the detector crystal and maintain its performance (this is more critical for the initial 500 volts). Following this powering up a short equilibration period should be allowed prior to performing detector calibrations or QC checks. This period is somewhat detector-specific.

SHIELDING

Detectors need to be shielded from external radiation, such as naturally occurring radionuclides emitted from building materials (particularly concrete). Shielding should be constructed of "old lead," and steel members should be used with caution, because steel fabricated after World War II may contain traces of ^{60}Co. The inner surfaces of these shields typically are lined with cadmium then copper (or a thick copper sheet) to reduce lead X-rays and backscatter photons originating from the shield walls.

BACKGROUND

Detectors have a certain background count rate from naturally occurring radionuclides, cosmic radiation, and the radioactivity in the detection equipment. Because of the processing of the germanium to remove impurities it has become a negligible source of background radiation. The specific background gamma radiation will depend on the amounts of the nuclides present and on the sensitivity of the detector to the specific gamma rays.

Ideally, the material used for shielding should itself be free of any radioactive material that might contribute to the background. In practice, this is difficult to achieve as most construction materials contain at least some naturally radioactive species (such as ^{40}K, members of the uranium and thorium series, etc.). The thickness of the shielding material should be such that it will absorb most of the soft components of cosmic radiation. This will reduce cosmic-ray background by approximately 25 percent. Cosmic-ray interactions in lead shields will produce lead X-rays that are shielded typically by cadmium and copper liners. Such a shield is referred to as a "graded shield." Six millimeters of OFHC copper also can be used to reduce the cosmic-ray produced lead X-rays without the cadmium liner. Shielding of beta- or gamma-ray detectors with anti-coincidence systems can further reduce the cosmic-ray or Compton-scattering background for very low-level counting.

The gamma-ray background spectrum for a germanium detector has two specific features. The first is the general shape of the background counts versus energy function. The shape can be described as a $1/(E_\gamma)$, or hyperbolic. Part of this response is because of the decrease in detector efficiency as energy increases. The second feature is the presence of a 0.511 MeV peak corresponding to annihilation radiation. This is because of the interaction of high energy gamma/ cosmic radiation with the lead shielding via the pair production effect. The size of this peak should be constant (in terms of counts per unit time) as long as radionuclides with gamma energies greater than 1.02 MeV are not present in the sample being counted. This peak and the general background can change under some unusual conditions (like solar flares, or the 11-year sun spot cycle).

TEMPERATURE AND HUMIDITY

Humidity can have significant effects on the many cable connections that germanium detection systems have. The change in moisture can affect cable connection impedance, which ultimately can affect peak shape. The counting room should be maintained at 40-60 percent relative humidity.

There are two separate temperature effects that can be seen. The first deals with the detector itself. The band gap in the germanium crystal is affected by the absolute temperature, so it is maintained at -196 °C using a cryostat. The cryostats are designed to have minimum thermal leakage. However, each crystal responds to different cryostat temperatures from low levels of liquid nitrogen in the dewar in which the cryostat is immersed. Many of the newer systems have low-level monitors that alert the analyst to replenish the supply of liquid nitrogen. For those that do not have feature, addition of liquid nitrogen to the dewar should take place routinely (usually about every 1–2 weeks). The detector should be allowed to equilibrate for at least one hour after the refill before it is used for analytical work.

The other temperature effect is that of the room environment on the electronics. Although the detector and the electronics may be on a conditioned line, the instability of temperature in the

room can cause the pre-amplifier, amplifier, and ADC/PHA portions of the system to respond erratically. The temperature of the room should be maintained in the 21–27 °C range.

15.6.3.2   Gamma Spectrometer Calibration

Most HPGe gamma-ray spectrometry systems are calibrated with mixed gamma-ray sources in a similar matrix and with the same geometric form as the samples to be analyzed. This requires the purchase of several different calibration sources. Commercial calibration sources 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 sources 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).

Counting efficiencies are determined by measuring a known quantity of the radionuclide(s) of interest within a similar matrix and with the same source-detector configuration as the sources requiring analysis (NCRP, 1978; ASTM, D3649). This eliminates any effect that might be caused by differences in standard and sample 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 test source (Coomber, 1975; ANSI, 1991).

MARLAP recommends that calibration data for gamma-ray spectrometry calibration be obtained from the National Nuclear Data Center at Brookhaven National Laboratory (www.nndc.bnl.gov/ nndc/nudat/). Data required for calibration are the half-life of the radionuclide, its gamma-ray branching ratio, and the probability of producing conversion electrons. These are readily available for common radionuclides, including ^{210}Pb, ^{241}Am, ^{109}Cd, ^{57}Co, ^{58}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-ray spectrometry calibration, see ANSI 42.14 (also see Section 16.3.1.6 on gamma calibration.)

Figure 15.9 shows an example of three different geometries that may be used for gamma counting the same sample configuration. It is necessary to calibrate each geometry for the detector since the distance from the detector has a significant effect on the number of photons that intersect the detector. This relationship is more significant for geometries or shapes that are close to the detector's active volume.

Table 15.7 shows the efficiency of different sample container configurations for a gamma-ray detector. The efficiencies cited are for a sample container placed in contact with the germanium detector surface. Counting efficiencies were obtained using a 55 percent HPGe detector (55 percent relative to a NaI(Tl) detector of 7.5×7.5 cm.).

Recently, calibrations of gamma-ray detectors using computer software and sample geometry modeling have been shown to be accurate when compared to a traditional mixed gamma ray

The dotted arrows represent the same solid angle, which subtends the detector from the different sample geometries. Sample shape and positioning will have a significant effect on the efficiency with which the detector "sees" the sample gamma rays.
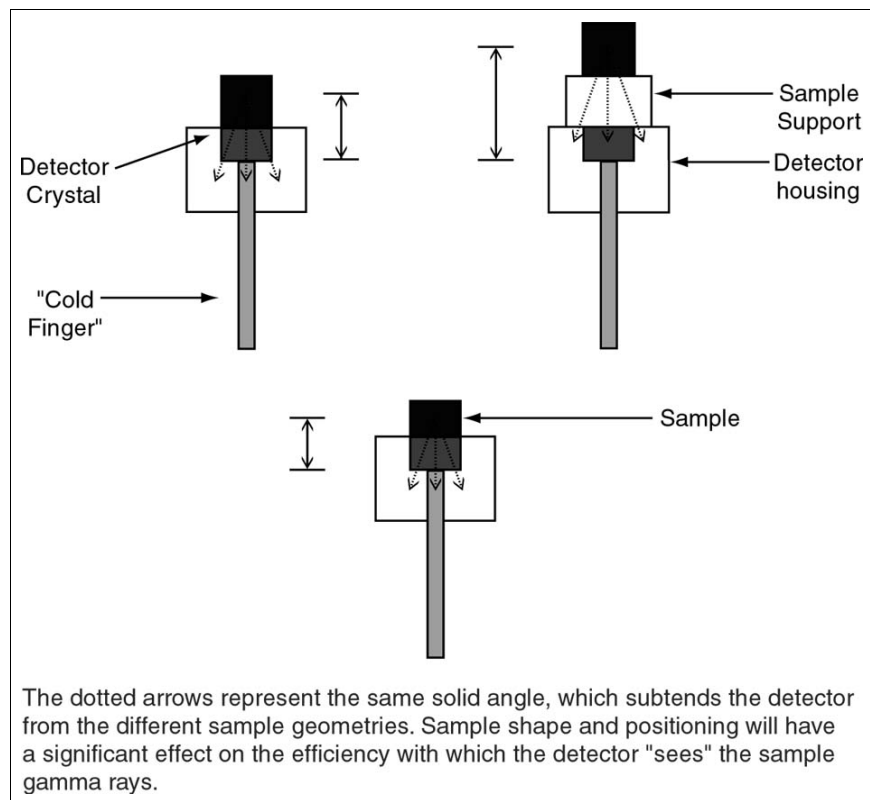
FIGURE 15.9 — Different geometries for the same germanium detector and the same sample in different shapes or position

source calibration (Mitchell, 1986; Hensley et al., 1997). An analytical advantage of this system is that the analyst may be able to analyze a smaller portion of an unknown than the size and shape used for a traditional calibration.

TABLE 15.7 — Typical percent gamma-ray efficiencies for a 55 percent HPGe detector[*] with various counting geometries

Energy (keV)	Filter Paper	50 cm³ Planchet	90 cm³ Al Can	600 cm³ Marinelli Beaker
60	15.6	14.6	11.6	5
88	15.2	14.2	11.3	7.4
122	15.1	12.6	10.2	8.4
166	12	9.6	8	7.9
279	9.3	7.4	6	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	3.1

Energy (keV)	Filter Paper	50 cm³ Planchet	90 cm³ Al Can	600 cm³ Marinelli Beaker
835	3.9	2.9	2.4	2.7
898	3.1	2.4	2.1	2.2
1115	3	2.3	1.9	2.1
1173	2.6	2	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 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.

15.6.3.3   Troubleshooting

Troubleshooting can fall into two separate arenas. One for the electronic performance of the system and the second for interpretation of the gamma-ray results. The former usually involves the assessment of routinely measured parameters and careful examination of the system hardware when measurements are out of the norm. The latter involves a more fundamental understanding of the interactions of radiation with matter and detectors, and may require deductive reasoning.

ELECTRONIC MECHANICAL EFFECTS

Gamma-ray spectrometry systems have many parameters that should be monitored routinely to establish the characteristics of the system. The following should be monitored on an appropriate frequency (as discussed in Section 18.5.6 of Chapter 18, *Laboratory Quality Control*):

- Peak centroid of standards vs. channel number;
- FWHM of peaks for at least three energies over the range of 100–2,000 keV; and
- Detector efficiency of a separate source (not the calibration source) with energies at high and low keV values.

These parameters form the basis for identifying problems with the detection system. Some examples of how these parameters are used to determine the cause of problems are listed here:

- FWHM of 1,173 keV peak normally is 2.0 keV and now is 3.0 keV. Peak broadening can be a sign of low liquid nitrogen level in the dewar or warming of the cryostat. This type of effect can occur when cryostat refills are based on routine, without consideration for sudden changes in ambient temperature.

- Centroid of 662 keV peak has continued to shift steadily towards lower channel numbers:

The spectroscopy amplifier may be aging and needs replacement.

- Spectrum collection appears erratic (stop and go): Moisture condensation on cable connections can be creating variable impedance problems. Check room humidity.

- Low energy "pile-up" on a quality-control or background count appears higher than normal: Room temperature may have increased causing an increase in thermionic/electronics noise.

- Efficiency of 121 keV peak is consistent but lower than normally expected for several days in a row. Look at the test-source positioning method used in the system. Often the same detector uses plexiglass sample platforms and Marinelli beakers without the platform. If the test-source platform has not been repositioned the same as it was for the calibration source (considering that rotational positions on the detector surface are different), efficiency will be affected.

RANDOM AND COINCIDENCE (CASCADE) SUM PEAKS

At high count rates, random sum peaks may occur. Two gamma-ray interactions may occur within the resolving time of the detector and electronics and are summed and seen as one pulse. For a detector of resolving time, t, and a count rate of A counts per unit time, the time window available for summing is 2At (since the count summed could occur as early as t before or as late as t after the other count) and the probability of another count at any time is simply A. Therefore, the sum count rate will be $2A^2t$ in unit time. Random summing is strongly dependent on the count rate A. If summing occurs, it can be reduced by increasing the sample to detector distance. 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, and not recording counts for the individual 2,000 and 1,000 keV gamma events. When the detector starts reporting more sum peaks than valid events, you have exceeded its count rate capability. Random pulse summing or pulse 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 reducing the number of events the detector sees (by moving the sample further away), collimating the sample, or using a smaller, less-efficient detector (the smaller the detector the shorter the charge collection time, which means a higher count rate limit). Modern electronics, both conventional analog and digital (pre-amplifiers, amplifiers, and analog-to-digital converters) are capable of processing 100,000 cps without any significant loss of peak resolution. This is because of the very short time constants (resolving time) these systems are capable of producing. Peak shifts also may occur with high count rates and short time constants.

Well counters that have very high efficiencies are prone to summing, because 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; 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. In this instance, a radionuclide in an excited state emits a gamma ray and de-excites to a lower energy level. The lifetime of the lower energy level is so short that the emission of a subsequent gamma ray from that state is anisotropic with respect to the first emission (the nuclear relaxation time between events is too short, and the gamma rays are emitted in the same direction from the nucleus). The second gamma ray is seen by the detector in the same timeframe as the first gamma ray. Co-60 is an example; 1,173.2 keV and 1,332.5 keV from consecutive, excited state, decay events may interact with the detector simultaneously, giving a 2,505.7 keV sum peak. Another example of cascade summing occurs when counting ^{22}Na close to the detector (Figure 15.8). The positron emitted by ^{22}Na creates a 511 keV gamma ray. When this gamma ray interacts with the detector in the same time frame as the emitted gamma ray following the positron emission, a 1,786 keV sum gamma ray is observed (511 + 1,275 keV). Cascade summing may be minimized by increasing the source-to-detector distance

ESCAPE PEAKS

Gamma-ray interaction with solid materials results in pair production formation (β^+ and β^-) when the energy of the incident gamma is greater than 1,022 keV. However, the β^+ particle can create certain artifacts by the way it interacts with matter. Once formed, the β^+ has a very short lifetime. It loses all of its kinetic energy to detector electrons in a time frame commensurate with the original event. When the β^+ particle annihilates it forms two 511 keV gamma rays. If both of these gamma rays escape the detector without interacting, a peak 1,022 keV lower than the FEP is seen. Sometimes only one of the gamma rays will escape the detector, and a peak at 511 keV lower than the FEP is realized. These two artifacts are referred to as double and single escape peaks, respectively.

The size of these peaks relative to the FEP is dependent only on the detector material and no other characteristics. The ratio to the FEP is constant and thus these peaks are usually only seen after very long count times or with very high activity samples.

MULTIPLETS AND INTERFERING GAMMA RAYS

A distinct advantage of using an HPGe detector is that it may be possible to analyze a sample for gamma emitters without radiochemical separation steps. This is possible because of the better resolution (FWHM) of the gamma-ray spectrometry system and the improvement in software, which can resolve gamma-ray peaks within a few keV of each other. For example, using a HPGe detector spectrometry system, the 1,115.5 keV photopeak of ^{65}Zn easily can be resolved from the 1,120.5 keV photopeak of ^{46}Sc. However, difficulties arise in quantifying the area under each photopeak when the two photopeaks are not separated by more than an energy differential equivalent to the FWHM peak resolution at that energy. When the differential of two gamma-ray energies is less than twice the FWHM, a single composite peak (wider than normal) may be observed in a spectrum. The composite peak is known as a "doublet" or "multiplet." The

resolution and quantification of photopeaks of a multiplet requires special software subroutines. In the previous example with ^{65}Zn and ^{46}Sc, a ^{214}Bi photopeak at 1,120.3 keV would form a multiplet peak with the 1,120.5 keV ^{46}Sc photopeak because the difference between the gamma-ray energies is less than the FWHM at 1,120 keV. In this example, a sufficient quantity of ^{214}Bi would generate an interfering gamma-ray photopeak for the ^{46}Sc photopeak, the analyte of interest. If an interfering gamma-ray peak is present, the analyst can employ one of three things:

- Find an alternate gamma line for the radionuclide where no interfering gamma ray exists;
- Allow the activity of the interfering gamma ray to decay (if it is shorter-lived) and then count the radioisotope of interest; or
- Perform radiochemical separation.

Many radionuclides emit more than one gamma ray. However, each gamma ray may not be emitted with each radionuclide decay event. This fraction of time that a gamma ray is emitted may be known as the fractional abundance or branching ratio. When a gamma ray is used to identify a radionuclide, and the radionuclide has other gamma rays that it emits, these other gamma rays should be present in the gamma ray spectrum (corrected for efficiency) in the same fractional ratio for the theoretical case. If this is not the case, then an interfering gamma ray may be present. For example, a gamma ray is found at 241 keV and potentially identified as ^{88}Kr. The fractional abundance of this line is 0.003. Kr-88 also has a gamma ray at 196 keV with a fractional abundance of 0.26. If this gamma ray is not present, or not present in the correct ratio, then an interfering gamma most likely exists. In this particular instance a likely candidate is ^{214}Pb (241.9 keV).

SPECTRUM DEGRADATION

Troubleshooting gamma ray spectra problems can be difficult. Gamma ray shape and positioning are the key characteristics that help to identify problems. The shape of a gamma-ray photopeak may appear to be Gaussian. However, it is best described by three different curves. A low-energy exponential, a middle Gaussian (about the centroid), and a high energy exponential (more drastic drop in events per energy than the low energy exponential). Upon close examination, the true gamma-ray peak will always appear to be "leaning" towards the low energy end. Listed here are some parameters that when changed cause specific effects that may be easily corrected. Some of these effects may take place during a sample count. If this happens, the effects may be more difficult to sort out.

Temperature. Changes in room temperature will affect the electronics for the amplifier and MCA units. The most common effect that can be seen from this is that the FWHM of the peak will increase (the peak will upon close up examination appear to be a true Gaussian). Usually this is most pronounced when the room temperature increases more than 3-4 °C. Maintaining the count room at a constant and moderate temperature will avoid this problem.

Humidity. Moisture within the gamma-ray detection system results from condensation on connectors. This can have irreproducible effects, because the heat generated by the electronics can cause the condensed moisture to evaporate. A common effect observed, which is related to humidity, is an irregular peak shape. A test or calibration source known to have only one gamma ray may appear to be a multiplet if humidity is effecting the system.

Voltage shifts. Changes in the 120 V AC power to the high-voltage power unit, which are not compensated for by a line conditioner, will cause the peaks to move. Thus gamma rays may appear at energies several keV different from where they are expected. The software will identify the gamma rays as radionuclides, but they will be unfamiliar to the analyst. This is the key to check line voltage changes. This may or may not cause a change in the FWHM since voltage changes may only occur at discrete times (the so called "5 o'clock effect").

Low Liquid Nitrogen. Gamma-ray FWHM will begin to increase and the low-energy pile up pulse rate will increase. The obvious fix is to add more liquid nitrogen to the dewar. However, if this happens unexpectedly (i.e., in between normal fillings), cryostat integrity or thermal contacts should be checked.

Vibration. High frequency vibration can establish electronic variations in the signals between the amplifier and ADC. One common effect is that the FWHM of the peaks will increase. Another effect is that "new" peaks that do not correspond to known radionuclides may appear. The vibration may be transmitted to the preamplifier/amplifier through the detector shielding or through the cryostat. Dampeners such as foam or rubber may help to reduce this problem.

15.6.4 Extended Range Germanium Detectors

The extended-range germanium detectors are constructed slightly differently than the normal HPGe coaxial detectors. Normally, the lithium-diffused junction (which is on the outside surface of the crystal) is about 0.5–1.5 mm thick. Also, these detectors will be encased in an aluminum detector housing. The combination of these two factors effectively shields the sensitive area of the detector from gamma rays with energies below about 40 keV. The extended range detector is a coaxial germanium detector having a unique thin-window contact on the top surface and a thin beryllium cryostat window, which extends the useful energy range down to 3 keV. The physical characteristics of the extended-range detector are shown in Figure 15.10.
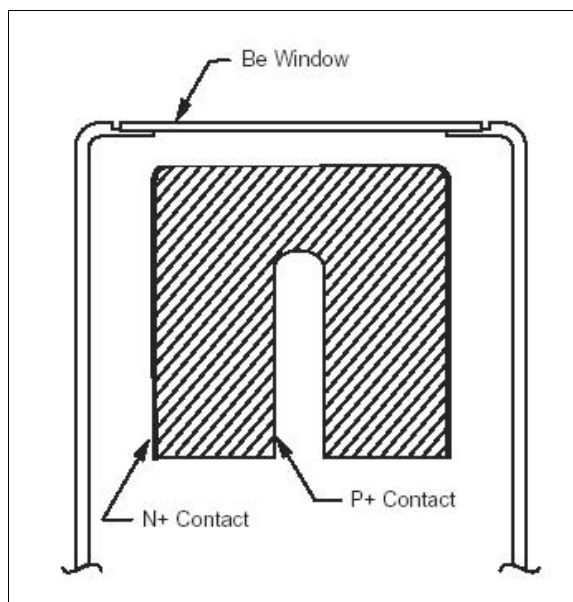
FIGURE 15.10 — Extended range coaxial germanium detector

15.6.4.1 Detector Requirements and Characteristics

The FWHM of this detector at 22 keV ranges from 0.7 (for a low efficiency detector) to 1.2 keV (for the higher efficiency detectors). The beryllium window allows for the passage of the low-energy gammas ray to the active detector area. This makes the handling of samples at the detector surface very important. It also means that if the sample container has a higher Z value than beryllium, the container may provide more shielding from gamma rays than the detector window.

Voltage requirements of the detector are similar to the HPGe detectors, and are specified by the manufacturer. The shielding requirements for this type of detector will be the same as for the standard coaxial detector. It is important to note, however, that since the range is extended into the X-ray region of elements down to aluminum, it would not be unrealistic to see X-rays from the interaction of sample gamma rays with materials of construction of the sample container, etc.

Similarly, the total background at low energies will be affected significantly, because the detector window will allow a greater number of photons to reach the detector surface (as beryllium does not shield as much as the traditional aluminum detector barriers). This also means that the ADC dead time may increase significantly because of the increased number of photons being processed by the system. Dead time increases should be monitored closely, because they will affect the quality of the peak shapes. Temperature and humidity considerations for these type detectors are similar to those of the standard HPGe detectors.

15.6.4.2 Detector Calibration

Calibration of extended-range germanium detectors is the same as for normal coaxial germanium detectors (Section 15.6.3.2, "Gamma Spectrometer Calibration"). However, since the active area allows quantification of gamma rays down to about 3 keV, additional gamma emitters with peaks in the range of 60 down to about 5 keV need to be used to perform calibration. One of the radionuclides that can serve this purpose is ^{109}Cd, which has a gamma peak at 88 keV and silver K_α X-rays (the electron capture decay converts the cadmium nucleus to a silver nucleus before the electron cascade) at 22 keV. One of the important characteristics of the detector is that the ratio of the 22 to 88 keV peak intensities should be about 20:1 for a properly operating system. Figure 15.11 shows a calibration curve for the extended range compared to the normal coaxial detector. The extended range detector has a discontinuity at 11 keV because of the germanium K-shell absorption edge.

Coincidence summing of X- and gamma-rays emitted from certain radionuclides should be considered during detector calibration. In many cases, radionuclide-specific calibrations are required, because coincidence summing effects for certain radionuclides having high X-ray emission rates produce lower than expected efficiencies for the gamma-ray energy.
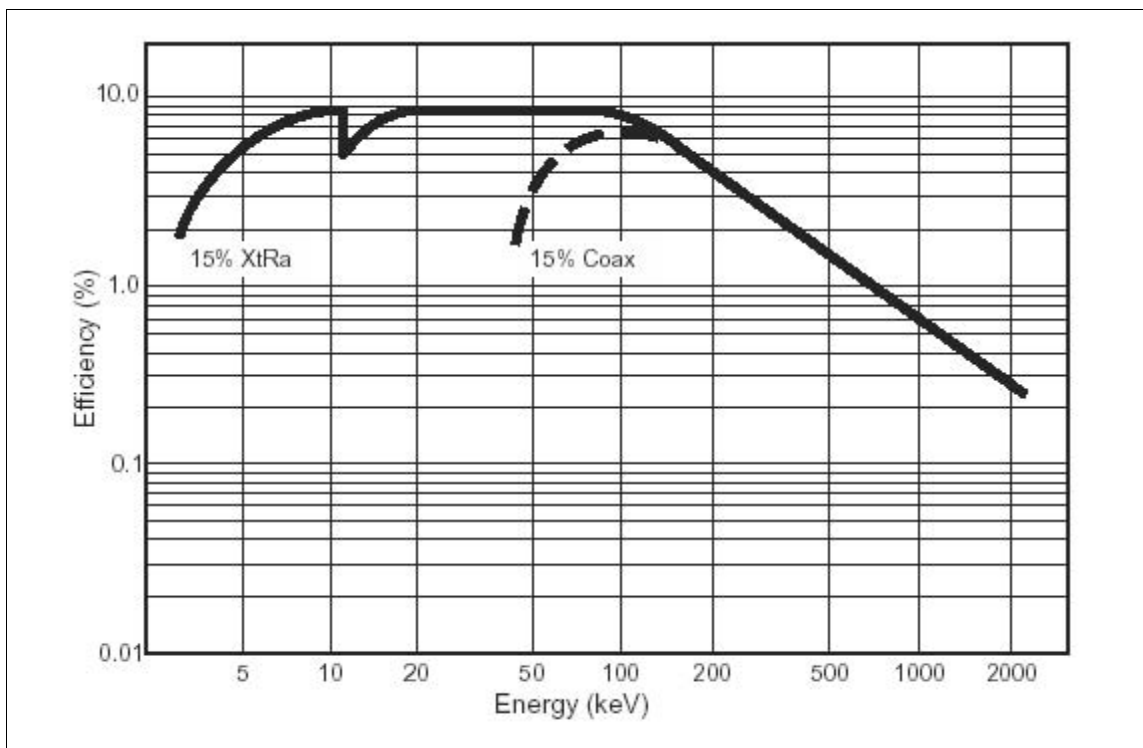
FIGURE 15.11 —Typical detection efficiencies comparing extended range with a normal coaxial germanium detector

15.6.4.3   Troubleshooting

Troubleshooting information in Section 15.5.3.3 ("Detector Calibration") applies to this detector as well. It should be noted, however, that because an extended range of energies is available, additional random sum peaks may be encountered that will be close in energy to the principal gamma rays. For example, if the source has ^{60}Co (1,332 and 1,173 keV peaks) and ^{109}Cd (22 keV peak) present, at high count rates additional peaks may be observed at 1,354 and 1,195 keV.

15.6.5 Special Techniques for Radiation Detection

15.6.5.1   Other Gamma Detection Systems

A variety of other methods and detectors are in use to analyze gamma radiation. Although they do not find general use in the analytical community, they are noted here.

OTHER GERMANIUM DETECTORS

The low-energy germanium (LEGe) detector has a thin beryllium window and a small detector

volume. The intent is to focus on the gamma-ray energies in the 10–200 keV range. The small volume reduces the efficiency to higher energy gamma rays allowing good resolution of low-energy gamma rays.

The reverse electrode germanium (REGe) detector changes the positioning of the N- and P-type materials on the detector crystal. The P-type material is on the outer periphery of the crystal where the significant interaction of the gamma rays with the crystal occur. This P-type junction is less susceptible to radiation damage. Thus, the REGe is best suited for high activity samples.

MIXED ELEMENT DETECTORS

Bismuth germanate ($Bi_4Ge_3O_{12}$, or BGO) is a very effective gamma-ray absorber because of the high average Z value from the bismuth. A BGO detector acts similarly to a scintillation detector but has only about 15 percent of the efficiency of a comparable size NaI(Tl). Its advantage over the NaI(Tl) detector is that it is nonhygroscopic and shock insensitive. Its major use is for when a high photopeak fraction needs to be measured (i.e., it yields a high peak-to-Compton ratio).

Cesium iodide 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 PMTs the yield for gamma rays is only about 45 percent of the NaI(Tl) type detectors.

Cadmium-zinc-telluride detectors do not have energy resolutions as good as HPGe, but are better than NaI(Tl) detectors. Their biggest advantage is their ability to operate at room temperature. Generally they are used for high activity sources since their size is generally small.

15.6.5.2   Coincidence Counting

In coincidence counting, two or more radiation detectors are used together to measure the same test source, and only those nuclear events or counts that occur simultaneously in all detectors are recorded. The coincidence counting technique finds considerable application in studying radio-active-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., 1981; 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, α–γ, 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 radionuclides 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 test source. Thus, the method reduces interference from other gamma emitters in the test source. 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; 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 sensitivies (Cooper et al., 1968). An example of an assay for plutonium content using passive thermal-neutron coincidence counting is given in ASTM C1207. Another example of passive thermal-neutron coincidence counting using a moveable californium source is given in ASTM C1316.

Coincidence counters normally are employed in radioanalytical laboratories for special purposes:

- For low-level measurements when the sensitivity of a beta- or gamma-counting system is inadequate,

- When spectrometric applications are needed to discern the emissions from several isotopes whose activities are very small; or

- For the standardization of radioactive sources by absolute counting (coincidence means).

Beta-gamma coincidence counting systems have been developed for the low-level measurement of ^{131}I in milk samples (McCurdy et al., 1980; Paperiello and Matuszek, 1975). The β-γ coincidence counting system reported by McCurdy et al. (1980) consisted of a 25.4 mm diameter, 1 mm thick Pilot B plastic scintillator optically coupled to a photomultiplier tube by a 12.5 mm plastic light pipe. The beta detector PMT was contained in an aluminum housing that inserted into a 100×100 mm NaI(Tl) well gamma-ray detector. The beta-gamma detectors were shielded by 100 mm of lead. The outputs from both detectors were coupled to separate timing single channel analyzers (TSCA) that produced fast positive digital logic output pulses when a detector signal satisfied the SCA voltage (energy) window. Since the decay time of the voltage pulse from the plastic scintillator detector is faster compared to a NaI detector pulse, the logic pulse of the beta scintillator was delayed by 200 ns. A coincidence pulse analyzer and a scaler were used to

detect and record the coincident beta and gamma events from the detected decay emissions of [131]I. The coincidence counting system had a β-γ coincidence background for ^{131}I of 0.00045 cps (0.027 cpm) and a detection limit of 0.4 pCi/L for a 1,300 second counting interval. Figure 15.12 shows the detector efficiency plots for a beta-gamma coincidence counting system (McCurdy et al., 1980).

A α-γ coincidence counting system for the alpha emitting isotopes of radium has been reported by McCurdy et al. (1981). The same β-
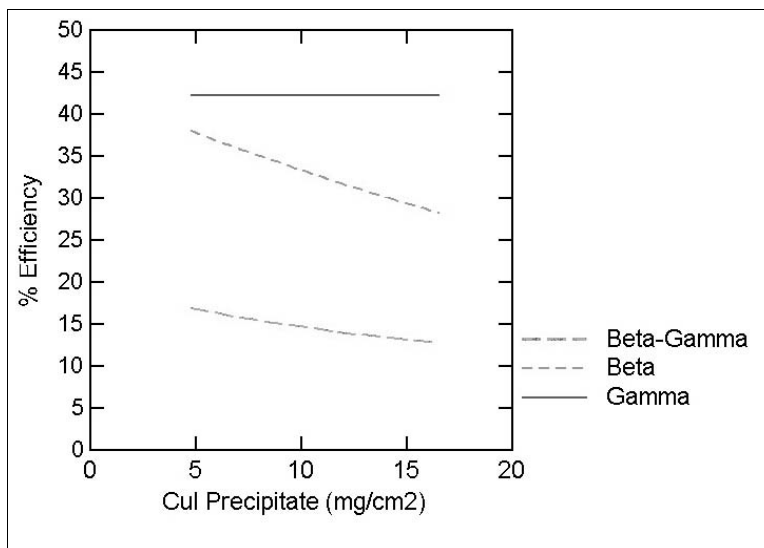
FIGURE 15.12 — Beta-gamma coincidence efficiency curve for [131]I

γ coincidence counting system used for the ^{131}I application was also used for the analysis of [228]Ra but the gamma-ray window was set for the gamma-ray photopeak for [228]Ac, the short-lived decay product of [228]Ra. For the α-γ coincidence counting application, the timing of output pulses of the TSCAs was changed to accommodate the long decay time of the alpha voltage pulse generated from the ZnS(Ag) alpha scintillator positioned next to the beta detector. The radium was coprecipitated with $BaSO_4$ and powdered ZnS(Ag) added to the final precipitate to form a 4π alpha detector. The Pilot B plastic scintillator was found to be transparent to the wavelength of the ZnS(Ag) light output. The gamma TSCA energy window was set for the 186 keV line of [226]Ra. The α-γ coincidence background was essentially zero for the 186 keV window over days to a week counting interval.

15.6.5.3   Anti-Coincidence Counting

Substantial background reduction can be achieved in beta and gamma counters by surrounding or covering the test-source 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 used 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 (1955) in his study of natural [14]C. The thick metal shielding (lead or iron) 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 test-source detector produce a count that is recorded with the total energy of the gamma ray (FEP). There are second-order effects that prevent complete elimination of Compton scattering, but the improvement is substantial (Perkins, 1965; Cooper et al., 1968).

15.7 Specialized Analytical Techniques

Certain methods employing analyte detection techniques other than nuclear-decay emissions have been successfully used for the measurement of medium to long-lived radionuclides. Two of the three methods to be described determine the number of atoms or the mass of the radionuclide(s) of interest. The other method involves neutron activation of a limited number of the long-lived nuclides. As a result of the unavailability of a neutron source, neutron activation analysis is typically outside the capability of most radioanalytical laboratories.

15.7.1 Kinetic Phosphorescence Analysis by Laser (KPA)

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 emitted light can be either fluorescence or phosphorescence. In either case, the detector is at right angles to the laser excitation. Fluorescent light is emitted immediately following ($<10^{-4}$ sec) the excitation of the complex. With phosphorescence, however, the emitted light is delayed, following the excitation. This enables the light source to be pulsed and the measurement to occur when the laser source is off, thus providing improved signal-to-noise over fluorescence. The light signal from organic material will decay promptly (since they have a relatively short lifetime) and will not be available to the detector, which is gated off. A pulsed nitrogen dye laser (0.1 to 0.5 mW range) often is used as the source, but other lasers can be used. Chloride and other ions can cause interference and may need to be removed before measurement.

KPA measures the rate of decay of the uranium or lanthanide characteristic energy. 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.

An excellent reference describing the theoretical and functional aspects of a KPA unit and its application to the measurement of the uranyl ion in aqueous solutions has been written by Brina and Miller (1992) The authors reported a detection limit for UO_2^{+2} in aqueous solutions as 1 ng/L and a linear response from the detection limit to 5 mg/L. Experiences using a KPA unit for a variety of matrices that include water, urine, dissolved air filters, stack scrubber samples, soil,

nuclear fuel reprocessing solutions and synthetic lung fluid were also reported. Matrices other than water may require dilution, preliminary sample dissolution and/or possibly chemical processing before analysis by a KPA unit. Consideration should be given to ensuring that the chemical yield for such processes is quantitative. Standard addition with internal standards may be needed for certain complex matrices.

There are several types of interferences that should be considered when using this method. The interferences can be differentiated into five categories: light absorption agents, such as yellow solutions and ferric iron; lumiphors, such as oils and humic acid; quenching agents, including alcohols, halides (except fluoride), and certain metals; competing reactions; and HCl. Chlorides interfere in the analysis by quenching the uranyl phosphorescence. Chemical interferences must be removed or their concentration reduced significantly by dilution to avoid inaccurate results.

KPA can be used to measure total uranium in water at concentrations greater than 0.05 μg/L (0.05 ppb). Samples above the KPA dynamic range of about 400 ppm can be diluted with dilute HNO_3 (1+19) prior to analysis. For the ASTM D5174 method, a 5 mL sample aliquant is pipetted into a glass vial, concentrated HNO_3 and H_2O_2 are added and the solution heated to near dryness. The residual is dissolved in 1 mL of dilute nitric acid, diluted with 4 mL of H_2O and a complexant is added. The 5 mL sample is analyzed by the KPA unit. Some reagents may have relatively short shelf life and need to be ordered accordingly. An interlaboratory study conducted for ASTM D5174 measured bias under 0.5 percent and between-laboratory precision (six laboratories) of 12 percent at a testing level of 2.25 ppb. For an individual laboratory, the relative precision was found to be about 4 percent at this level.

An automated KPA has also been applied to monitor uranium in stack filters and probe washes at a nuclear facility (Mann et al., 2002). The KPA was adapted to incorporate an automatic sampler and syringe pump permitting the unattended analysis of 60 samples. Methods were developed to eliminate interferences from inorganic and organic compounds. The reported detection limit was better than 1 ppb. Typical precision was about 5 percent.

Ejnik et al. (2000) have reported using KPA for the determination of uranium in urine. In this application, the researchers processed 10 mL of urine by successive and multiple dry (450 °C for 4 hours) and wet (HNO_3 and H_2O_2) ashing treatments prior to sample analysis. A detection limit of 50 ng/L and an observed concentration range between 110 and 45,000 ng/L were reported for this application.

15.7.2 Mass Spectrometry

Mass spectrometry is being used more frequently for the analysis of medium- to long-lived radionuclides. There are three types of mass spectrometers being used today for the radioanalytical applications including radiobioassay, process and waste stream characterization, effluent analysis and environmental sample analyses. The most readily available mass spectrometer for a

radioanalytical laboratory is an inductively coupled plasma-mass spectrometer (ICP-MS). Some of the various ICP-MS units commercially available include single- and multi-collector magnetic-sector ICP-MS and quadrupole ICP-MS. These bench-top units are commercially available at a reasonable price. The other two types of mass spectrometers (accelerator mass spectrometers and thermal ionization mass spectrometers—see Sections 15.7.2.2 and 15.7.2.3) typically are found at national laboratories and universities or institutes, are expensive, and require special facilities including a clean-room environment for certain applications. Instrument descriptions and application references for mass spectrometry can be found in several sources (McDowell, 1963; Date and Gray, 1989; Platzner, 1997; de Laeter, 2001).

Time-of-flight plasma mass spectrometers have just recently appeared on the market. They have not yet compiled a historical record of performance that would permit reliable comparison with the ICP-MS. Similarly, Fourier-transform mass spectrometers are primarily used for research and cannot yet be considered practical for routine radiochemical analysis.

15.7.2.1   Inductively Coupled Plasma-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 nuclear-decay emission-counting techniques in the radiochemical analysis laboratory. General references describing ICP-MS instrumentation, advantages and limitations of the methodology, and the potential applications of ICP-MS to radionuclide measurements include Date and Gray (1989), Platzner (1997), ASTM (STP1291), ASTM (STP1344), and Ross et al. (1993).

For very long-lived radionuclides (those with half-lives over 10,000 years, e.g., $^{234/235/238}$U, $^{239/240/244}$Pu, ^{99}Tc, ^{129}I, ^{237}Np), ICP-MS may be faster and more sensitive than nuclear-decay emission analyses. In addition, sample preparation for ICP-MS can avoid some of the analyte separation and purification steps required for nuclear-decay emission analyses, 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 and ^{239}Pu vs. ^{240}Pu). This information is frequently useful in determining the age or origin of materials (ASTM C758, C759, C799). Typically, ICP-MS can typically detect femtograms (10^{-15} g) of a nuclide. Depending on the nuclide and required detection limit, the radioanalytical front-end chemistry may have to be conducted in a clean room or clean hood environment. In addition, high purity reagents may be required for certain radionuclides (e.g., uranium isotopes).

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 instru-

ments are employed for their higher signal/noise ratio, and therefore superior detection limits.

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 [233]U signal to precisely the same extent. Final quantification relies on measuring the ratio of unknown (here the [235]U signal) to the known ([233]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.

For environmental sample analysis, the elements or radionuclide of interest are normally concentrated and isolated chemically. However, for the measurement of uranium in ground and surface water, where the natural levels may be much greater than the instrument's detection limit, the samples may be diluted and then analyzed under certain conditions. Currently, there are two ASTM methods for the analysis of ^{99}Tc, [230]Th, and [232/234/235/238]U in soils, C1310 and C1345. Natural background uranium concentrations in soil is between 3 and 5 µg/g in most geographical regions. The background thorium concentrations are slightly higher. The detection limits for uranium and thorium by the C1345 method are well below the background concentrations of these elements. The method described in C1310 has reported detection limits in soil for ^{99}Tc, [230]Th and [234]U as 12, 4, 0.7 Bq/kg, respectively. In addition, Uchida and Tagami (1999) proposed a rapid separation method using an extraction chromatographic resin for ^{99}Tc in sea- and ground water that has a detection limit of 0.3 mBq/L for 2 L samples. They also reported an ICP-MS method for the analysis of ^{99}Tc in soil that was used to measure the ^{99}Tc levels from worldwide fallout at concentrations of 5–30 mBq/kg dry (Tagami and Uchida, 1999). Ihsanullah and East (1993) published methods for the analysis of ^{99}Tc by ICP-MS for environmental media including water, soil, and marine algae with an ICP-MS detection limit of 0.004 ppb (2.52 mBq/mL).

ICP-MS has been used to analyze [239]Pu and [240]Pu in ocean sediment (Petullo et al., 1994). The analysis involved dissolution of a 20 g sample, followed by precipitation of the actinides, dissolution of the precipitate, and anion exchange for Pu isolation. A [242]Pu tracer was used for the chemical yield determination. Reported detection limits for [239]Pu and [240]Pu were 30 mBq/kg and 80 mBq/kg, respectively.

More recent environmental applications include the analysis of nuclides with intermediate half lives, including [90]Sr (Taylor et al., 2002) and [226]Ra (Kim et al., 1999; Lariviere, et al., 2002) in environmental media, and [135/137]Cs (Epov et al., 2002) in waste waters. Lariviere et al. (2002) reported for [226]Ra a detection limit of 7.4 Bq/L (0.2 nCi/L) without elemental pre-concentration methods to remove interferences and 0.2 pg/L (0.007 Bq/L or 0.2 pCi/L) with a 50 times pre-concentration and elemental isolation. Their method required low sample volume (25 mL), had rapid chemistry (30 minutes) using extraction (extractant resin) chromatography, and a two

minute/sample instrument measurement. Kim et al. (2002), using their chemical concentration and isolation methods, reported detection limits for water and soil of 0.00019 Bq/L and 0.75 Bq/kg, respectively.

ICP-MS has also been used for radiobioassay applications for ^{239}Pu and isotopic uranium in urine samples. The Brookhaven National Laboratory used ICP-MS to measure the ^{239}Pu concentration in urine samples from Marshall Island residents. Inn et al. (2001) evaluated the capabilities of BNL to analyze urine samples by ICP-MS in an intercomparison study to measure ^{239}Pu in synthetic urine. In the study, BNL pre-concentrated and isolated the plutonium in the synthetic urine through established and validated chemical techniques prior to analysis by mass spectrometry. Pu-242 was used as a yield monitor with each analysis. For four testing levels between 18.5 nBq/mL (18.5 µBq/L) and 278 nBq/mL (278 µBq/L), the mean of the BNL replicate (five samples) measurements for the four test levels had biases ranging from -6.8 to -20 percent. The 1σ precision for the five replicate measurements per test level was under 13 percent for all levels. The detection level was calculated to be 1,600 nBq per 200 g sample.

Lawrence Livermore National Laboratory (LLNL) has used ICP-MS coupled with chemical concentration (phosphate coprecipitation) and isolation to analyze isotopic uranium in urine samples (Hotchandani and Wong, 2002). A ^{233}U yield monitor was used with each sample (200–1500 mL). ASTM C1379 provides a test method for the analysis of urine for ^{235}U and ^{238}U by ICP-MS. Ejnik, et al. (2000) reported ^{235}U detection limits of 14 ng /L for natural uranium and 50 ng/L for depleted uranium (uranium with 0.2 percent ^{235}U) in urine, given a uranium detection limit of 0.1 ng/L. The researchers were able to determine correctly and accurately the ^{235}U : ^{238}U isotopic ratio for depleted and natural uranium in 10 mL urine samples having total uranium concentrations between 150 and 45,000 ng/L. The 10 mL samples had been treated by multiple and comprehensive dry and wet-ashing processes prior to analysis.

Nguyen et al. (1996.) reported a method for the simultaneous determination of ^{237}Np, ^{232}Th and the uranium isotopes in urine samples using extraction chromatographic sample preparation (TRU column) in conjunction with ICP-MS. They reported detection limits , using pre-concentration methods for 1/10 daily urinary excretion volume, of 13 µBq (8 x 10^{-4} dpm), 1.7 nBq (1×10^{-7} dpm), 33 nBq (2×10^{-6} dpm), and 7 nBq (4×10^{-7} dpm) for ^{237}Np, ^{232}Th, ^{235}U, and ^{238}U, respectively.

Lee et al. (1995) conducted an intercomparison study to evaluate the capability of the various alpha spectrometric and mass spectrometric methods for determining ^{237}Np in artificial urine samples. For this study, results from 10 different methods were evaluated in terms of bias and precision at two concentration levels (50 mBq/kg and 3.3 mBq/kg) as well as detection limits. At the time of the study, the best detection limit reported for alpha spectrometric and mass spectrometric methods were very similar (0.1 mBq/kg). However, the range of the reported detection limits was more consistent for the alpha spectrometric methods compared to the mass spectrometric methods.

15.7.2.2   Thermal Ionization Mass Spectrometry

Thermal ionization mass spectrometers (TIMS) rely on ionization from a heated filament rather than on a plasma. They provide more precise measurements than routine quadrupole ICP-MS but require substantially more operator involvement, leading to markedly reduced sample throughput compared to ICP-MS units. In addition, because of the design of most TIMS units, a limit of four samples per batch can be analyzed sequentially without reloading another set of samples. TIMS systems exist at the national laboratories and the National Institute of Standards and Technology. These units are large and are usually considered too expensive for commercial laboratory operations. In addition, facilities housing TIMS may have ventilation systems equivalent to a Class 100 clean room, depending on the application. In some cases, the initial radioanalytical chemistry is conducted in a class 100 clean room or hood.

TIMS has been successfully applied to the analysis of ^{239}Pu, ^{240}Pu, ^{235}U and ^{238}U in a variety of matrices. However, initial radioanalytical methods must be performed to isolate and concentrate the radionuclides from the initial sample. A radionuclide or isotopes in the concentrated solution would be electrodeposited on the filament used in the TIMS. For ^{239}Pu, Los Alamos National Laboratory (LANL) electrodeposits plutonium from a purified sample onto a TIMS filament with dihydrogen dinitro-sulfato-platinate. A larger quantity of platinum is then electrodeposited over the plutonium to provide a diffusion barrier that dissociates plutonium molecular species and provides high ionization efficiency. Detection limits in the femtogram range are typical, resulting in a ^{239}Pu concentration of 600 nBq/200 g sample (Inn et al., 2001). In a recent interlaboratory comparison study evaluating the capabilities of mass spectrometric methods for the analysis of ultra low quantities of ^{239}Pu and ^{240}Pu in urine (McCurdy et al., 2002), LANL's TIMS method had an estimated detection limit of 6 µBq/L. For ^{240}Pu in the samples, the detection limit was estimated to be 20 µBq/L. LANL observed good precision (about 4 percent relative standard deviation) for ^{239}Pu test levels at 28 µBq/L and above. The ^{240}Pu measurements were less precise than the ^{239}Pu measurements, 11.9 percent and 21.2 percent respectively for 32 and 16 µBq/L.

TIMS has been used to evaluate the isotopic ratio of ^{238}U : ^{235}U in urine samples. In a study reported by D'Agostino et al. (2002), five participating laboratories were provided 12 synthetic urine samples (1 kg each) containing varying amounts of natural and/or depleted urine. Various mass spectrometers were used, including sector-field ICP-MS, quadrupole ICP-MS, and TIMS. The TIMS and quadrupole ICP-MS had similar detection limits: 0.1 pg for total uranium (based on ^{238}U) and about 15 pg for a ^{238}U : ^{235}U ratio of 138 (natural abundance). The TIMS was able to measure ^{238}U : ^{235}U ratios in ranges between 138 and 220 for three test levels of 25 to 100 ng/kg, 100 to 350 ng/kg and greater than 350 ng/kg.

Additional information and radionuclide measurement applications of TIMS can be found on the Los Alamos National Laboratory and Savannah River Site websites, http://pearl1.lanl.gov/ bioassay/tims.htm and http://srs.gov.

15.7.2.3   Accelerator Mass Spectrometry

Accelerator mass spectrometry (AMS) systems are routinely used by a limited number of national laboratories, universities and institutes rather than commercial or government radioanalytical laboratories. These systems are technically sophisticated, expensive and fairly large, requiring extensive laboratory space and facilities. Currently in North America, five organizations have AMS systems primarily for earth science, bioscience and environmental studies. The organizations include Woods Hole Oceanographic Institution, University of Toronto, Purdue University, University of Arizona, and LLNL.

In AMS, negative ions made in an ion source are accelerated electrostatically through a field of millions of volts. The accelerated ions pass through a thin carbon film or a gas to destroy all molecular species. After passing through a low- or high-energy mass spectrometer and various filters, the resulting ions slow to a stop and dissipate their energy in a gas ionization detector. The identity of the individual ions is determined from the ions' rates of deceleration, with the lighter ions decelerating more rapidly than the heavier ions. For AMS analysis, solid samples in the 0.1 to 1 mg mass range are pressed into sample holders.

AMS has been used for geological, biological, and environmental applications for several decades. In the1980s, AMS replaced the traditional method of scintillation counting for precise radiocarbon dating. A ^{14}C detection limit of 200 nBq (5×10^4 atoms) is typical. Tritium, used extensively as a tracer in biological and oceanographical research, can be analyzed routinely by AMS with a detection limit of 20,000 nBq. AMS can be used to measure the following low-mass cosmogenic radionuclides for earth science applications: ^{10}Be, ^{26}Al, ^{32}Si, ^{36}Cl and ^{41}Ca. In addition, ^{63}Ni, ^{129}I, and $^{239/240}$Pu are routinely analyzed by AMS at LLNL. Table 15.8 (McAninch, 1999) provides the detection limits for these radionuclides.

TABLE 15.8 — AMS detection limits for selected radionuclides

Nuclide	Detection Limit (nBq)	Detection Limit (10^5 atoms)
^{3}H	20,000	1
^{14}C	200	0.5
^{10}Be	4	3
^{26}Al	1	0.4
^{36}Cl	3	0.3
^{41}Ca	200	8
^{63}Ni	45,000	2
^{90}Sr*	~100,000	~7
^{99}Tc*	~30,000	~600
^{129}I	1	1
$^{239/240*}$Pu	~1,000	~10

* proposed

McAninch and Hamilton (1999) compares the capabilities of the various mass spectrometric methods and fission tract analysis for the analysis of [239]Pu and the other actinide elements. The report includes a description of the facilities at the LLNL Center for AMS as well as the detection methods used. Additional information can be obtained online at http://cams.llnl.gov.

Recently, AMS has been used in radiobioassay to measure the [239]Pu in urine samples. McCurdy et al. (2002) evaluated LLNL's AMS technology for [239//240]Pu bioassay measurements during an interlaboratory comparison study. LLNL's AMS method had an estimated detection limit of 6 µBq/L. For [240]Pu in the samples, the detection limit was estimated to be 15 µBq/L. LLNL observed good precision (under 2 percent relative standard deviation) for [239]Pu test levels at 28 µBq/L and above. The [240]Pu measurements were less precise than the [239]Pu measurements, about 27 percent for 16 µBq/L and above test levels.

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16 DATA ACQUISITION, REDUCTION, AND REPORTING FOR NUCLEAR-COUNTING INSTRUMENTATION

16.1 Introduction

This chapter provides information and guidance, primarily for laboratory personnel, on data acquisition, reduction, and reporting for nuclear-counting instrumentation processes. Its intent is to provide an understanding of the many operational parameters that should be addressed in order that the data developed and reported are compliant with project planning documents (Chapter 4), considered valid (Chapter 8, *Radiochemical Data Verification and Validation*), and usable for their intended purposes (Chapter 9, *Data Quality Assessment*). 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 that are used 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 nuclear-counting instrumentation. 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 16.2, and those that are specific to a given type of instrumentation are covered in the appropriate section describing that instrument. Detailed descriptions of the instruments discussed in this chapter are provided in Chapter 15, *Quantification of Radionuclides*.

Once test sources have been prepared and counted using laboratory measurement instruments (Chapter 15), the basic information generated by the instrument should be processed and reduced to data that can be reviewed, verified, validated, and interpreted in accordance with project planning documents and analytical statements of work (SOWs; also see Chapters 5, *Obtaining Laboratory Services*, and 7, *Evaluating Methods and Laboratories*). Data reduction is primarily mathematical in nature while data reporting involves the presentation of the results of the data acquisition and reduction

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[1] The term "test source" means the radioactive material prepared to be introduced into a measurement instrument, and "laboratory sample" means the material received by the laboratory for analysis. Thus, a test source is prepared from laboratory sample material in order to determine its radioactive constituents. A "calibration source" is a source prepared for the purpose of calibrating instruments.

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 detector 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). In any case, the reduction process should continue by calculating the combined standard uncertainty (Chapter 19, *Measurement Uncertainty*).

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 proportional counter whose only output is from an electronic scaler, and the available data consist of total counts or count rate. On the other extreme, some laboratory counting instruments with computer components produce outputs consisting of radionuclide concentration, uncertainty, and other information. 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 or analytical SOWs 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 that 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 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.

16.2 Data Acquisition

Data acquisition in this context refers to the process of collecting the basic information produced by nuclear-counting instrumentation. 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 transferred electronically or manually to the next data-reduction step. Electronic transfer should be employed as often as possible, as long as the software process has been verified and validated to perform correctly in this function. Software responsible for electronic data transfer should be validated and verified initially, and any changes verified and validated. A manual recheck of some portion of the data analysis should be performed on a routine basis (e.g., annually).

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.

16.2.1 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 or in the analytical SOW. 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, adjustments to instrument operating parameters (e.g., count times) 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 turnaround 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, radiological holding time, and sample turnaround 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 test-source generation

• 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.

16.2.1.1   Counting Duration

The standard uncertainty of a measurement with total number of observed counts, N, using Poisson counting statistics, equals the square root of N (as further explained in Chapter 19). The relative fractional uncertainty of the measurement of N is then $1 / \sqrt{N}$. The expected value of N is proportional to the length of the counting period; so, increasing the counting duration, which is a controllable factor, can reduce the relative uncertainty of the measured counts. The analyst then should select counting durations for the sample and the blank that are sufficient to meet the project objectives for detection capability and method uncertainty. An alternative to selecting the counting duration, available on many radiation counting instruments, is to count until a preset number of counts is obtained.

Note that the overall measurement uncertainty for the final analytical result usually depends on many factors besides the counting uncertainty; so there is a limit to the improvement that can be made by adjusting counting times alone.

16.2.1.2   Counting Geometry

The counting efficiency of a radiation detector depends upon (among other things) the geometry of the source and detector arrangement, i.e., the solid angle subtended at the detector by the source (see Chapter 15, *Quantification of Radionuclides*). 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 quantification requirements 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 source-to-detector distance. Choices are to be made among those for which the detector has an established efficiency calibration.

16.2.1.3 Software

The use of properly developed and documented computer software for data acquisition and reduction can enhance 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 radionuclide levels.

When selecting software, one should thoroughly review the data reduction algorithms. 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, consisting primarily of counting data (total counts or count rate). These data should be manipulated by external systems to convert them to the form required by planning documents. The external system that 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 identifier (ID), collection date, sample mass or volume processed, 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 that 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.

The software data reduction and reporting functions should be verified to perform as expected. For example:

- Manual calculations and software calculations performed on the same raw data should produce the same analytical results; and

- Calculation of activity using secondary/tertiary gamma rays of a radionuclide should consistently validate the activity determined from the primary gamma ray.

16.2.2 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:

$$R_C = \frac{C_G - C_B}{\varepsilon \cdot V \cdot Y \cdot K_C \cdot e^{-\lambda t_1}} \tag{16.1}$$

where:
R_C = radionuclide concentration at a reference time (i.e., time of collection) (Bq/L or Bq/g)
C_G = gross counting rate (source + background) (cps)
C_B = counting rate of the blank (cps)
ε = detector efficiency for the radionuclide being measured (cps or Bq)
V = volume or mass analyzed (L or g)
Y = chemical yield (when appropriate)
e = base of natural logarithm
λ = radioactive decay constant for the radionuclide (reciprocal time units)
t_1 = time lapse from sample collections to beginning of source count (units consistent with λ)
K_C = correction for decay during counting and is:

$$K_C = \frac{1 - e^{-\lambda t_C}}{\lambda t_C} \tag{16.2}$$

where:

t_C = clock time (total time during which counting occurs) of counting (units consistent with λ). Clock time, live time, and dead time are discussed below.

Equation 16.1 calculates the radionuclide concentration at the time of sample collection. It compensates for the fact that short-lived radionuclides may experience significant reduction in activity during counting, when the counting duration is a significant fraction of the half-life.[2] For long-lived radionuclides ($t_{1/2}$ > 100 times the counting time), the term K_C approaches unity and may be ignored. The efficiency used in this equation may be obtained from the specific radio-nuclide whose concentration, R_C, is to be determined or it may be obtained from an efficiency curve that plots detector efficiency against energy. In the latter case, the emission probability per decay event, E_e, (also called "abundance," "percent abundance," or "branching ratio") of the particle or photon being counted must be considered. This is required because the energy dependent efficiency, ε_e, is developed in terms of the fraction of particles or photons detected divided by the number emitted at that energy. Thus, if the radionuclide emission being determined during the counting of a test source has an abundance less than 100 percent, an adjustment should be made to Equation 16.1, as shown in Equation 16.3:

$$R_C = \frac{C_G - C_B}{E_e \cdot \varepsilon_e \cdot V \cdot Y \cdot K_C \cdot e^{-\lambda t_1}} \tag{16.3}$$

Most modern instrument systems contain software to perform data manipulations that convert basic counting information to a form that can be compared to the project data quality objectives, or at least to begin or promote this process. Certain sample-specific information should be manually entered or transferred to the system electronically in order to perform the necessary calculations.

"Live time" is the time period that the analyst chooses to count the sample. "Dead time" is the period that the counting system is unable to process multiple detection events within the resolving time of the analog-to-digital converter (ADC) plus storage in the correct memory channel. All counting systems have some dead time. Live time plus dead time is called "clock time." For environmental samples, or when using gamma spectroscopy or liquid scintillation

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[2] If several half-lives of the radionuclide elapse between sampling and analysis, decay-correcting the result to the time of sampling increases both the measured concentration and its uncertainty. When a result that is statistically indistinguishable from zero is decay-corrected in this manner, the corrected result may be positive, negative, or zero, but the magnitude is often so large that it causes concern to data users. See Attachment 14A, "Radioactive Decay and Equilibrium."

systems, dead time is usually negligible, because decay events (even with multiple radionuclides present) randomly occur far enough apart (Canberra, 1993). In these cases, the live time is the same as elapsed time (elapsed time sometimes is referred to as "real" or "clock" time). However, as the sample activity increases, the probability of two decay events happening within a short time of each other also increases. When the first event is being processed by the ADC, the ADC will not accept another pulse until the output of the ADC is stored in the correct memory channel (the period of dead time). If a second event occurs during the detection and count-system analysis of the first event, the second event is not counted. Some counting systems counting systems compensate for this by using the "preset time," which does not advance during this detector processing period. (Preset time thus is synonymous with live time.) Many systems have meters that indicate percent dead time. This can be expressed by Equation 16.4.

$$\% \text{ Dead Time} = \frac{\text{Clock Time} - \text{Live Time}}{\text{Live Time}} \times 100 \qquad (16.4)$$

Increasing the live time by this percentage yields the clock time. Although clock time and live time are very close, clock time should always be used in ingrowth or decay calculations, especially with radionuclides whose half-lives are significant with respect to the counting interval.

The best method of compensating for high dead time samples is to either dilute the sample or use less of it for the analysis. High dead times can cause other problems with the counting systems such as peak shaping and signal recognition, which can affect results.

16.3 Data Reduction on Spectrometry Systems

Software is available for resolving alpha, gamma (including X-rays), and liquid scintillation spectra and for performing the attendant functions such as calibration, energy alignment, background acquisition and subtraction, and quality control (QC) 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 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). 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 of the source being analyzed and to the count time.

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) and unfolding (Tsoulfanidis, 1983). Computer programs for analyzing alpha and gamma spectra are available from several sources (Decker and Sanderson, 1992). A method of performance testing of gamma analysis software is given in ANSI N42.14.

16.3.1 Gamma-Ray Spectrometry

Gamma-ray spectrometry on environmental samples requires the use of gamma spectral analysis software for any reasonable degree of accuracy and detection capability. (Reference to gamma rays and their detection in this context also includes X-rays from radionuclide decay.) 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 QC 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 radionuclides 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; USPHS, 1967).

Gamma rays interact with matter in three ways: by photoelectric effect, Compton scattering, or pair production (Tsoulfanidis, 1983). These interactions within a gamma detector (usually high-purity germanium or sodium iodide; see Chapter 15) result in varying amounts of the gamma-ray energy being absorbed. Only one—the photoelectric—results in the total energy being absorbed in a single interaction. The photopeaks in Figure 16.1 result from the processing of the detector signal through the linear circuitry and the multichannel analyzer.
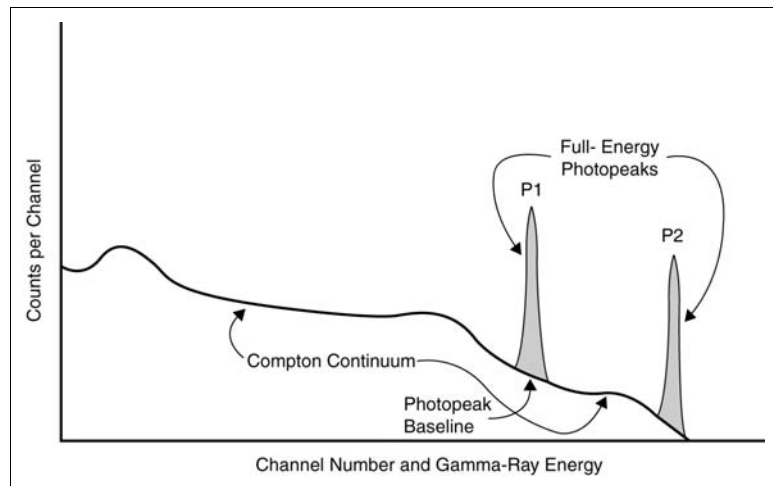
FIGURE 16.1 — Gamma-ray spectrum

As can be seen in the figure, a lower-energy photopeak (P1) may be displaced upward by combining with the accumulated counts from the Compton continuum, generated from other possible higher-energy photopeaks (P2) and background radiation. Each photopeak has a basic Gaussian shape (Gilmore and Hemingway, 1995). It may be described with the baseline counts removed from each peak channel (Quittner, 1972) by:

$$f(x) = A\,e^{-(x-p)^2/2\sigma^2} \tag{16.5}$$

where:

   $f(x)=$ the expected number of counts in any channel x
   x $=$ the channel number
   A $=$ the peak amplitude (counts in the centroid channel)
   p $=$ the peak centroid channel
   σ $=$ the standard deviation of the Gaussian peak

(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 $N = 1.064\ A\ \Gamma$.)

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 of the photopeak is proportional to the number of photoelectric events detected. 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 16.2.

16.3.1.1 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 Hemingway, 1995) 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. If only the regions of interest technique is used to assess the concentration of a radionuclide, it is still important to assess the presence of other radionuclides. For example, when determining ^{134}Cs (at the 604.7 keV peak), a false positive

Flow Step	Input Parameters
Define Sample Parameters ←	Sample ID, Batch ID, Nuclides of Interest, Volume/Weight w/uncertainty, Sample Geometry, Wet/Dry Ratio, Reference Date, QC Batch Index, Activity and Mass/Volume Units, Sample Collection Start/Stop…
Define Acquisition Parameters ←	Bias Voltage, ADC Gain, Amplifier Gain, Shaping Times, Filter Parameters, Energy Calibration, Shape Calibration, Acquisition Presets…
Acquire Spectrum	
Locate Peak Energies ←	Search Region, Threshold/Sensitivity, Tolerance, Regions of Interest, Library…
Determine Net Peak Areas ←	Peak Area Region, Continuum Parameters, Background Subtraction, Peak Rejection Criteria, Fitting Parameters, Multiplet Resolution Parameters…
Nuclide Identification ←	Nuclide Identification Region, Library, Tolerance, Threshold/Sensitivity, Efficiency Calibration, Decay Correction Parameters…
Activity Correction ←	Interference Library, True Coincidence Library, Efficiency/Geometry Parameters, Peak-to-Total Calibration…
Report →	Corrected Nuclide Concentrations, Measurement Uncertainties, MDC Calculations, List of Unidentified Peaks, Quality Assurance Tracking, Action Level Monitoring…

(Adapted from Gilmore and Hemingway, 1995; ORTEC/Ametec, 2002; Canberra, 2002.)

FIGURE 16.2 — Gamma-ray analysis flow chart and input parameters

result or high bias might be realized for the ^{134}Cs, if ^{125}Sb (606.6 keV) were present.

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 radionuclides. 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.

REGIONS OF INTEREST (ROI) METHOD

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 16.1). This method of spectral analysis may be more applicable to alpha rather than gamma-ray spectrometry.

GAUSSIAN FUNCTION DERIVATIVE METHOD

As previously stated, the photopeak has a basic Gaussian shape; in reality it is collected, stored, and presented in a histogram format. Mathematically, it is represented by an exponential on the low- and high-energy sides and Gaussian in the middle. The most widely used peak identification technique was proposed by Mariscotti (1967). This technique uses derivatives of the Gaussian function 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.

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 Hemingway, 1995).

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 base-line contribution leaves only positive counts within a photopeak. Although the scan function is normally Gaussian in form, other forms may be applied (Gilmore and Hemingway, 1995).

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 that 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 para-meters. Peak searches may be standard or directed (Canberra, 1994). In a standard search, all identified peaks are assigned to a radionuclide according to the nuclide energy values contained in a radionuclide energy library. In a directed search, the user specifies the energies and radio-nuclides over which the search is performed. If reporting a specific radionuclide is required, the directed search is appropriate; however, some radionuclides could go unreported if only a directed search is performed. Nuclides with multiple gamma rays may have several (but not all) gamma rays identified in the library. Depending upon user-selected criteria in the software, peak matches to library listings may be for a single line of the nuclide or multiple lines. An example is ^{60}Co, with gamma rays of equal intensity at 1,173 and 1,332 keV. A software option may be selected so that both gamma rays must be found for the positive identification of the ^{60}Co radio-nuclide. In this case, if only one of the peaks was found (as can occur for very low radionuclide concentrations), ^{60}Co would not be listed in the final analysis report.

In order to identify gamma peaks and radionuclides correctly, the user should select a radio-nuclide-energy library corresponding to the correct sample matrix or to those radionuclides in the sample based on the origin of the sample (e.g., SOW- or project-identified radionuclide list, soil samples, power plant effluent samples, etc.). For example, a radionuclide energy library for soil samples will include the gamma-ray energies associated with the radionuclides in the naturally occurring uranium and thorium decay chains. However, using this library to evaluate spectra for reactor coolant water samples having short-lived fission or activation products would be inappropriate, because some observed gamma peaks may not be identified and other observed gamma peaks may be misidentified as naturally occurring radionuclides. A radionuclide energy library may also be tailored according to the half-life of the expected radionuclides. Use of such a library avoids identification of a radionuclide whose half life would prohibit its presence in a sample.

16.3.1.2   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 Hemingway, 1995). 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 with 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 that 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 energies of gamma rays that 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 Hemingway, 1995).

16.3.1.3 Definition of Peak Centroid and Energy

Once a peak has been detected, the centroid of the peak will be defined, since it will rarely be located at exactly a whole channel number. The centroid will be used to represent the gamma-ray energy and should be calculated to the fraction of a channel. An algorithm used to calculate the centroid value may be expressed as (Gilmore and Hemingway, 1995):

$$\text{Centroid} = \frac{\sum C_i i}{\sum C_i} \tag{16.6}$$

where C_i is the number of counts in the ith channel.

In order to assign a gamma-ray energy value to the peak centroid channel position, the analysis program refers to a previously established energy calibration file. The detector's response to the full range of gamma energies should be established by counting one or more sources having a number of well-defined gamma rays over the range of energies emitted by the radionuclides in the calibration source. This calibration source most often is a "mixed-nuclide source" with certified emission rates, so that it also may be used for an efficiency calibration. The mixed-nuclide source is counted on the detector, being sure to accumulate sufficient counts in the peaks to obtain good statistical precision, and an energy-versus-channel relationship is established. The operator will be required to provide information on the peaks to be used and their exact energies.

With modern spectrometry systems, the relationship between energy and channel number is nearly linear. Both linear and quadratic fits have been included in available spectral analysis programs.

16.3.1.4 Peak Width Determination

In order to calculate the area under the peak, an estimate of the peak width is required, unless the analysis program is operating in the region-of-interest mode. The width of a photopeak is normally quoted in terms of its FWHM (see also Section 18.5.3.2, "Peak Resolution and Tailing"). For a discussion of peak width (resolution) and the factors affecting it, see Chapter 15.

There are several ways to determine the peak boundary. These are:

(1) A Gaussian shape is assumed and some number of standard deviations (2 or 3) are 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 (Figure 16.1).

The determination of FWHM requires an assumption of peak shape, and for gamma-ray spectrometry, the peak shape is assumed to be a Gaussian function. 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 Hemingway, 1995) and described by:

$$w = a + bE \qquad (16.7)$$

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 may be more appropriate to assume a peak shape that 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 16.3. Some spectroscopy programs have algorithms to fit peaks with lower energy tailing.
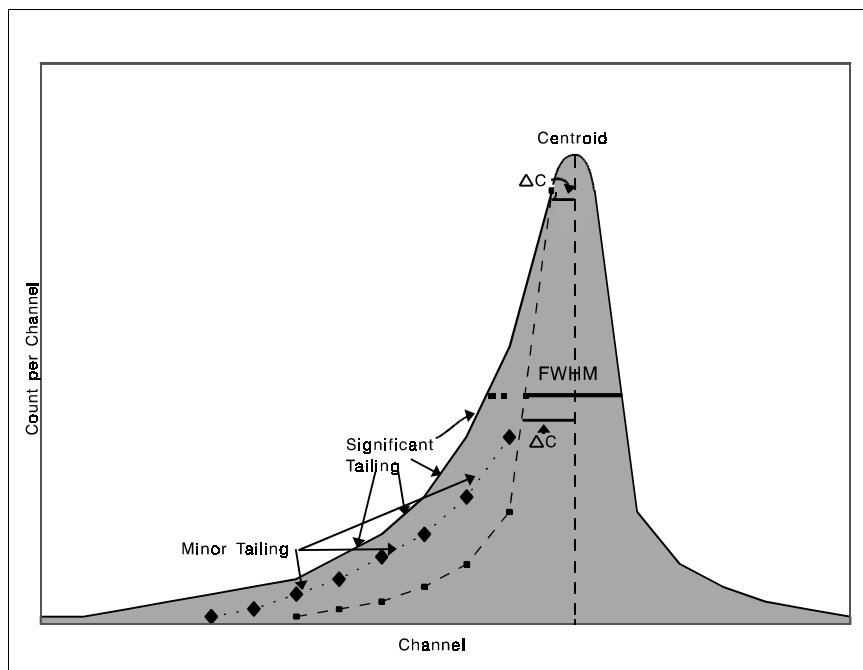
FIGURE 16.3 — Low-energy tailing

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 16.8), and those that are affected by tailing are modified according to Equation 16.9 (Koskelo et al., 1996):

$$y(x) = \begin{cases} A\,e^{\dfrac{-(x-p)^2}{2\sigma^2}}, & x \geq p - \Delta C \qquad\qquad (16.8) \\[2em] A\,e^{\dfrac{\Delta C(2x - 2p + \Delta C)}{2\sigma^2}}, & x < p - \Delta C \qquad\qquad (16.9) \end{cases}$$

where:

x	=	the channel number
A	=	the peak amplitude
p	=	the peak centroid channel
ΔC	=	the tailing factor (the distance from the centroid to the point where the tailing joins the Gaussian peak)
σ	=	the standard deviation of the Gaussian peak ($\approx$ FWHM / 2.355)

It should be noted that tailing may have many causes:

• Electronics temperature changes due to room temperature variation;

- Interferences from other gamma rays whose energies are <1 FWHM from the centroid;
- Phonic interference from vibration (e.g., a turbine);
- Detector degradation; or
- Detector temperature changes due to liquid nitrogen level.

These concerns should be corrected rather than trying to compensate for them mathematically using a correction factor.

16.3.1.5   Peak Area Determination

For single peaks sitting on a Compton continuum, two methods of peak area determination are available. The less complex method is the addition (integration) of the number of counts per channel in each of the channels considered to be within the peak limits, and subtracting the natural background and Compton contribution to those same channels (Baedecker, 1971; Loska, 1988). However, this is rarely simple since the photopeak is usually offset by a baseline continuum whose contribution is not easily determined. While the background may be subtracted by the spectrometry program, the Compton continuum will be estimated by the software and then subtracted. This estimation is often based on the number of counts per channel in those channels immediately above and below the photopeak region as shown in Figure 16.4 (after Gilmore and Hemingway, 1995).
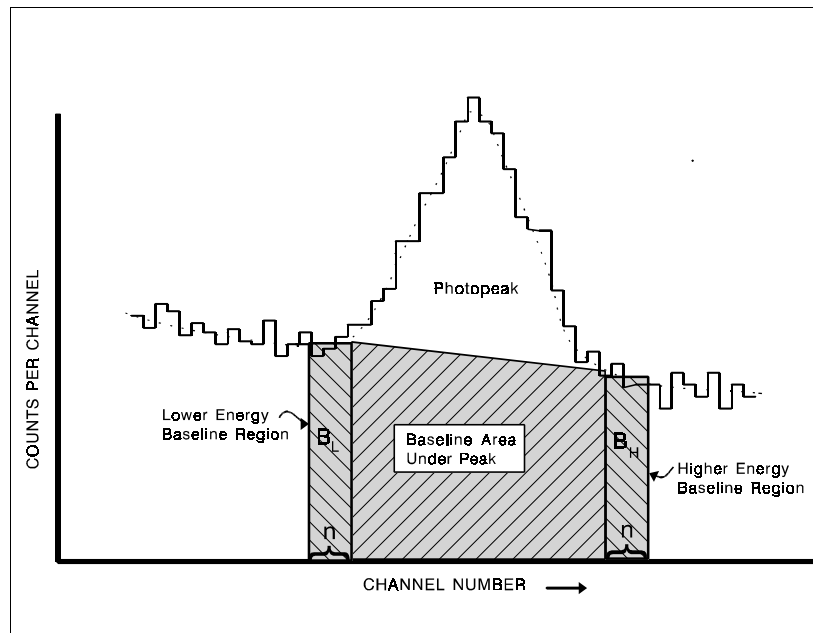
FIGURE 16.4 — Photopeak baseline continuum

The baseline contribution is then estimated as:

$$B = \frac{N}{2n}(B_L + B_H) \qquad (16.11)$$

where:

B = the number of counts attributed to the baseline
N = number of channels in the peak
n = the number of baseline channels considered on each side of the peak for calculating B_L and B_H
B_L = the sum of the number of counts in the baseline region on the low-energy side
B_H = the sum of the number of counts in the baseline region on the high-energy side

In practice, the baseline continuum appears to have a step beneath the peak (Gilmore and Hemingway, 1995), as illustrated in Figure 16.5.
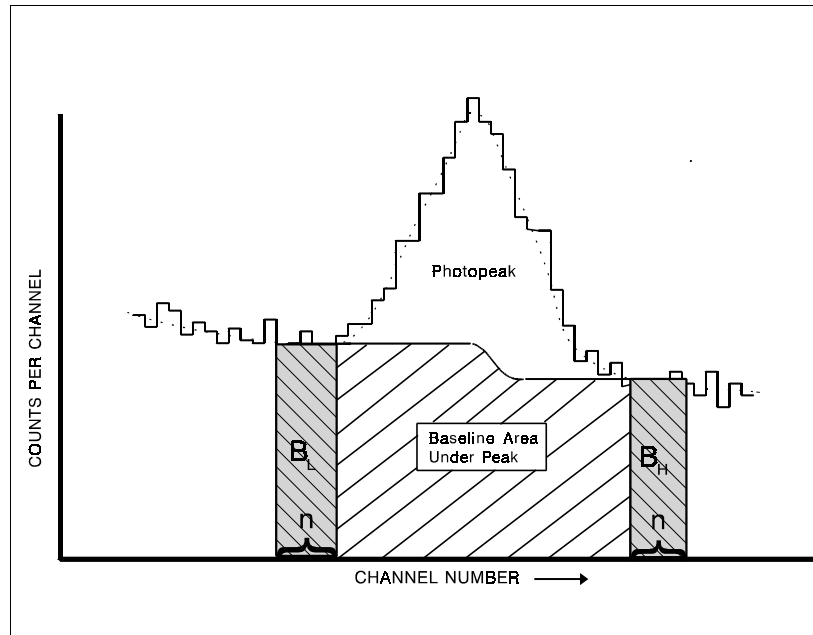
FIGURE 16.5 — Photopeak baseline continuum-step function

This type of function is estimated by:

$$B = \sum_{i=1}^{N} \left[\frac{B_L}{n} + \frac{B_H - B_L}{nG} \sum_{j=1}^{i} y_j \right] \qquad (16.12)$$

where:

B = the number of counts attributed to the baseline
B_L = sum of counts in the baseline region on the low-energy side

B_H = sum of counts in the baseline region on the high-energy side
y_j = counts per channel in channel j
G = gross counts in the peak
N = number of channels in the peak
n = number of channels in each of the two baseline regions

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 and McCullough, 1983). Background is often subtracted prior to the fitting process (Loska and Ptasinski, 1994).

16.3.1.6   Calibration Reference File

Both energy and efficiency calibrations are required for gamma-spectrometric analysis. These calibrations require a source whose gamma-ray emission rate is known and traceable to a national standard, and whose gamma-ray energies are well-defined. "Mixed radionuclide" standards, containing eight or more gamma-ray energies (from a variety of radionuclides) are commercially available for performing these spectrometric calibrations. Information required for proper energy and efficiency calibrations include:

• Radionuclide;
• Activity at the analysis date and time (or a specified reference date);
• Analysis date and time;
• Half-life;
• Energy;
• Energy tolerance (energy window expressed as ± keV);
• Gamma-ray emission per decay event (or "branching ratio");
• Emission-rate uncertainty; and
• Desired activity units.

This information usually is included on the calibration source certificate provided by the manufacturer. Calibration files are created using the software and methods prescribed by the instrument manufacturer. One of the factors important to efficiency and energy calibrations that results from this process is the FWHM. This is a function of gamma-ray energy and is used in assessing peak shapes and areas in different regions of the energy spectrum. The values for FWHM from the gamma rays in the standard are also used to establish acceptable tolerance limits for gamma rays in the analyte corresponding to the energy regions of the calibration source.

16.3.1.7   Activity and Concentration

In order to convert the counts under a photopeak to activity, an efficiency calibration should be performed on the detector for each test-source geometry. 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:

$$\varepsilon = \frac{C_r}{D}$$
(16.13)

where:
   ε = efficiency (cps or γps)
   C_r = cps measured under the area of the photopeak
   D = gamma-ray emission rate of source (γps)

The efficiency versus energy curve developed in most gamma software packages is in the form of a polynomial. One such form is:

$$\ln \varepsilon = \sum_{i=0}^{n} b_i \cdot [\ln E]^i$$
(16.14)

where:
   ε = full peak efficiency
   n = degree of the polynomial
   b_i = coefficient as determined by calculation
   E = the energy of the photopeak

The efficiency curve for HPGe detectors is comprised of three distinct regions: a low-energy curve (up to about 120 keV), a middle-energy curve (from about 120 to 661 keV), and a high-energy curve (> 661 keV). Frequently, manufacturer-installed software can be used to generate a single continuous efficiency curve from the three separate regions.

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.

16.3.1.8   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, which is due to the simultaneous emission of several 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-ray emissions from different atoms being detected almost simultaneously. If two gamma rays interact with the detector within the charge collection time of the detector or the resolving time of the amplifier, a count will occur in a single channel somewhere else in the spectrum equal to the sum of the two deposited energies. Random summing can occur for any pair of events, such as photoelectric with photoelectric, 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 that are distorted by summing (Gilmore and Hemingway, 1995). However, even with pile-up rejection random summing will still be present. A mathematical correction for random summing is given by:

$$A_T = A e^{2R\tau}$$
(16.15)

where:
  A_T = the true peak area (counts)
  A = the observed peak area (counts)
  R = the mean count rate of the total spectrum (cps)
  τ = the resolving time of the electronics (s)

If unknown, the resolving time can be estimated by a method similar to that described in Gilmore and Hemingway (1995).

True coincidence summing is a source of error when a source contains nuclides that emit several 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.

True coincidence summing can result in the loss of counts from photopeaks that are in

coincidence, and an apparent loss in the number of events detected at those energies. The sum peak also may be an emitted gamma ray. In this case, it would appear that more counts are present than expected at the sum-peak energy based on other peaks from the same radionuclide. 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 Hemingway, 1995). Some data have been published that 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.

16.3.1.9 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.

$$u_c = \sqrt{u_P^2 + u_V^2 + u_\varepsilon^2 + u_U^2 + u_F^2 + u_D^2} \tag{16.16}$$

where:
  u_c = combined standard uncertainty
  u_P = component of combined standard uncertainty due to the net peak area determination
  u_V = uncertainty component for the volume or mass determination
  u_ε = uncertainty component for the efficiency determination
  u_U = uncertainty component for the unfolding routine for multiplets
  u_F = uncertainty in the branching factor from the decay scheme for the radioactive emission being measured
  u_D = uncertainty in the decay constant of the radionuclide

Each of these factors may have a number of components of uncertainties included, for example, the net peak uncertainty:

$$u_P = \sqrt{u_G^2 + u_B^2 + u_E^2 + u_I^2} \tag{16.17}$$

where:
u_G = the uncertainty component for the gross counts in the peak
u_B = the uncertainty component for the baseline subtraction
u_E = the uncertainty component for the background peak subtraction
u_I = the uncertainty component for the coincidence summing correction

The calculations of combined standard uncertainty typically are performed by the gamma-ray spectrometry software. It should be noted that not every available software package will incorporate all the listed uncertainty contributions listed.

16.3.2 Alpha Spectrometry

This section deals with alpha-spectrum reduction as applied to semiconductor detectors. The range of alpha particles in air is only a few centimeters, and their energy degrades significantly only after a few millimeters. Therefore, alpha spectrometry is conducted in a partial vacuum and on extremely thin sources prepared by electrodeposition or coprecipitation. Typically, an alpha spectrometry system is set up to generate spectra from such thin sources that cover an alpha energy range between 4 and 10 MeV (see Chapter 15).

The number of full energy peaks is usually not large, three to four, in an alpha spectrum, and they are normally well separated in energy. This, coupled with the fact that the test source subjected to counting has gone through a chemical separation (Chapter 14), makes the radionuclide identification relatively simple when compared to gamma-ray spectrometry. However, it is still of great benefit to have alpha spectrometry software to identify radionuclides, subtract background, perform calibrations and energy alignments, determine radiochemical yields, and perform and track QC functions. In production laboratories where hundreds of alpha spectra may be generated each week, it is almost imperative that alpha spectra are resolved by properly designed computer software. An alpha spectrum produced by a semiconductor detector by the counting of a thin source containing ^{234}U, ^{238}U, ^{239}Pu, and ^{241}Am is shown in Figure 16.6.
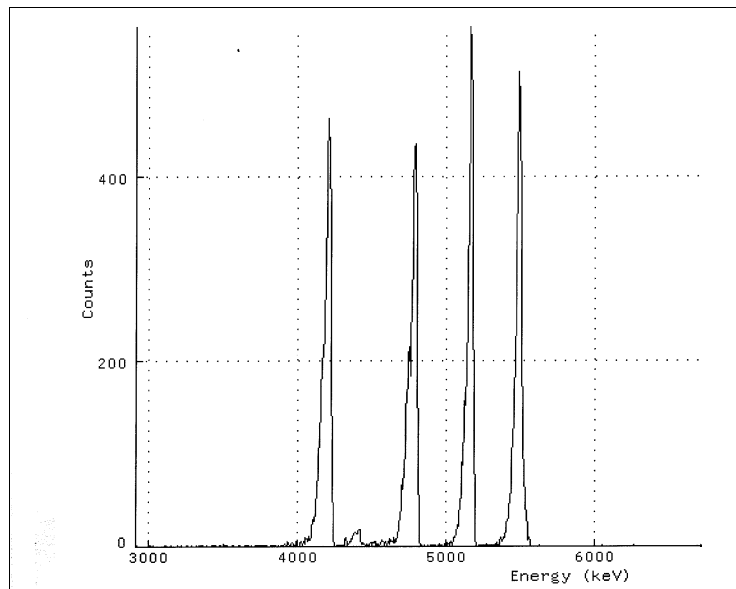

FIGURE 16.6 — Alpha spectrum
(^{238}U, ^{235}U, ^{234}U, $^{239/240}$Pu, ^{241}Am)

The shape of each of the five peaks in the figure appears superficially Gaussian but actually differs from the pure Gaussian model for a number of reasons. One reason is that each of the alpha-emitting radionuclides emits alpha particles at more than one energy. So, each apparent peak is actually a combination of several peaks, whose energies are too close together to be resolved by the spectrometer. A second reason is that each peak has a low-energy tail caused by degradation of the energies of alpha particles as they pass through matter. Very thin, flat, nearly massless sources tend to produce the smallest tails. A third reason is that some peaks also have noticeable high-energy tails, which can be caused by the summing of alpha-particle energies with the energies of conversion electrons associated with the alpha decay. Note that the baseline for all the alpha peaks is essentially zero. An alpha-particle spectrum differs from a gamma-ray spectrum in that it does not have a background component comparable to the Compton continuum.

Spectral analysis programs usually have routines to identify full-energy peaks. In the case of alpha spectrometry, because the number of alpha peaks is limited and their energies are well known, a simple ROI-type of analysis usually is performed. Peak-fitting programs are available and may be beneficial when peak overlap is of concern. The alpha-peak deconvolution algorithms should take into account the low-energy tailing (Equation 16.9). The algorithms that 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 the discussion on tailing in Section 16.3.1.4, "Peak Width Determination"). These programs should be applied with caution to spectra where the peak tails are misshapen or non-normal. The uncertainty due to the fitting algorithm can create unexpected results. The goodness-of-fit at the top of the alpha peak and at the low-energy tail should be reviewed carefully before accepting their results. If the algorithm is not providing reasonable results, the analyst may choose to seek alternatives to these algorithms to improve spectral resolution. These may include counting the sample at a distance farther from the detector or performing additional chemical separations to improve radiochemical purity.

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. However, it is important to establish QC limits for the alpha resolution parameter for the test sources being analyzed. For example, the alpha resolution should be held to less than 90–100 keV FWHM in order to prevent significant overlapping between the ^{243}Am tracer (11 percent at 5.233 MeV and 88 percent at 5.274 MeV) and the ^{241}Am peaks (13 percent at 5.443 MeV and 85 percent at 5.486 MeV). The test source typically is counted to achieve at least 1,000 counts (3 percent uncertainty) in the ^{243}Am tracer peak, which should be sufficient to estimate the alpha resolution. A laboratory may remount (microprecipitation method) or replate (electroplate method) the test source if the resolution exceeds an established QC limit.

Given these qualifications, the spectral analysis software performs essentially the same functions as 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 calculation, documentation, and QC purposes. The general analysis sequence for alpha spectrometry is discussed briefly below.

If a standard reference material is used for a tracer in each sample and an accurate determination of the yield is not required, an efficiency calibration is not necessary. 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 at the analysis date and time (or a specified reference date)
• Analysis date and time
• Half-life
• Energy
• Energy tolerance (energy window expressed as ± keV)
• Alpha-particle emission per decay event (or "branching ratio")
• Emission rate uncertainty
• Activity units desired

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. Some projects may require the reporting of the detector efficiency and chemical yield separately for each sample. For such cases, a one-time, initial calibration typically is determined and reported for each detector in use. When a calibration source contains several radionuclides with certified activities, a weighted mean efficiency should be calculated for the full-energy peaks and used as the alpha efficiency for a given detector (Chapter 15). The weighting factor would be the inverse of the variance (one over the square of the combined standard uncertainty) in the calculated detector efficiency for a radionuclide (Chapter 19).

The efficiency for alpha particles varies only slightly with energy, within the range of alpha

energies usually encountered (4-10 MeV). 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 15).

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 or from a protocol file. The yield, if required, is then computed by the use of an efficiency that has been determined previously during an efficiency calibration process. The radionuclide concentration is then calculated by[3]:

$$R_{C_i} = \frac{C_{R_i}}{\varepsilon_e \cdot V \cdot e^{-\lambda_i t_1}}$$

(16.18)

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 or Bq)
V = volume or mass analyzed (L or g)
e = base of natural logarithm
λ_i = radioactive decay constant for the radionuclide (reciprocal time units)
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:

---

[3] For short-lived alpha-emitting radionuclides (e.g., [224]Ra), a correction factor is needed for decay during counting. See Attachment 14A, "Radioactive Decay and Equilibrium."

- Assuring that the alpha peaks fall within the ROIs;
- Confirming the absence of unexpected peaks (contamination);
- Verifying that there are no interfering peaks;
- Confirming that peak centroids are within requirements (energy alignment);
- Verifying that all requirements are met with regard to FWHM (if possible) and chemical yield; and
- Checking units and sample aliquant information.

The FWHM of a given peak may depend greatly on the source preparation. However, since an ROI-type of peak search is normally used, and the limits of the peak determined by the setting of the ROI rather than some algorithm, the peak width definition is not significantly affected by reasonable peak broadening. As a precautionary measure, the above review of each test-source spectrum assures that the peaks appear within the ROIs. Alpha spectrometry analysis software allows for the adjustment of the ROIs to account for peak broadening and slight displacement. A review of the FWHM of the alpha peaks, as calculated by the software, will also reveal peak broadening due to matrix effects and poor test-source preparation.

16.3.2.1   Radiochemical Yield

Alpha spectrometry test sources are usually prepared by radiochemical separation and the chemical yield may be less than 100 percent. Therefore, a radiochemical tracer, which is an isotope of the radioactive species for which the analysis is being performed, may be added to the sample prior to preparation and radioanalysis. The tracer is normally a certified standard solution whose recovered activity is determined during the alpha spectrometric analysis in the same manner as the activities of the isotopes for which the analysis is being performed. The radiochemical yield is then calculated by the spectral analysis program according to:

$$Y = \frac{A_R}{A_S}$$
(16.19)

where:
    Y = radiochemical yield
    A_R = calculated activity recovered
    A_S = certified activity added (decay corrected to time of counting)

The calculation of the chemical yield is normally performed by the alpha spectrometry analysis software using operator input information relative to the alpha energy and abundance, activity, uncertainty, and date of certification of the radiochemical tracer.

For some types of radionuclide analyses, no suitable alpha-emitting radionuclide may be available for use as a chemical yield tracer. In this case, the chemical yield may be determined by some other method, such as beta counting, and the resulting yield value provided to the alpha

analysis program so the source activity may be calculated from the alpha spectrometry data.

When a certified 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.

16.3.2.2   Uncertainty Calculation

The calculation of the combined standard uncertainty for alpha spectrometry is similar to that for gamma-ray spectrometry as reported in Section 16.3.1.8 above. One additional source of uncertainty that 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

$$u_c(R_{C_i}) = \sqrt{\frac{u^2(C_{R_i})}{\varepsilon_e^2 V^2 e^{-2\lambda_i t_1}} + R_{C_i}^2 \left(\frac{u^2(V)}{V^2} + \frac{u^2(\varepsilon_e)}{\varepsilon_e^2} \right)}$$ (16.20)

or

$$u_c(R_{C_i}) = \sqrt{\frac{u^2(C_{R_i})}{\varepsilon^2 Y^2 V^2 e^{-2\lambda_i t_1}} + R_{C_i}^2 \left(\frac{u^2(V)}{V^2} + \frac{u^2(\varepsilon)}{\varepsilon^2} + \frac{u^2(Y)}{Y^2} + \frac{2 u(\varepsilon, Y)}{\varepsilon \cdot Y} \right)}$$ (16.21)

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 or Bq)
  V =   volume or mass analyzed (L or g)
  e =   base of natural logarithm
  λ_i =   the radioactive decay constant for the radionuclide (reciprocal time units)
  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 16.20 generally is easier to implement.

16.3.3 Liquid Scintillation Spectrometry

16.3.3.1 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 various 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 (Section 15.4.5.4), procedures for other beta- and alpha-emitting radionuclides have been developed over the years (Holm et al., 1984; Harvey and Sutton, 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 proportional counting (Section 16.4) and alpha semiconductor counting (Section 16.3.2).

16.3.3.2   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).

16.3.3.3   Pulse Characteristics

Excited triplet and singlet energy states are formed by the fluor molecules when ionizing radiation interacts with the scintillation cocktail. The excited singlet states dissipate their energy very rapidly and produce short lifetime decay pulses, whereas triplet states lose their energy more slowly, resulting in longer lifetime pulses. Because alpha particles have a higher linear energy

transfer than gamma or beta radiation, they produce a higher ratio of triplet to singlet excitation states and therefore have a longer pulse duration. Differences in the decay time and shape of the decay pulse are the basis for discriminating alpha particles from beta and gamma radiation in liquid scintillation counting (Passo and Kessler 1992; Passo and Cook 1994).

16.3.3.4   Coincidence Circuitry

Most modern liquid scintillation counters employ two photomultiplier tubes 180 degrees apart for the detection of pulses. The light produced when ionizing radiation in the test source interacts with the scintillation cocktail is emitted in all directions. A sample event should therefore produce electronic pulses in both photomultiplier tubes simultaneously, or in coincidence.

Electronic noise pulses are produced randomly by the photomultiplier tubes, but the probability that both tubes will produce noise pulses simultaneously is very low. An electronic gate can be set to allow only pulses that are in coincidence to be registered. The rejection of random pulses keeps background counts produced by electronic noise to a minimum. Similarly, the probability of background radiation (such as cosmic radiation) yielding an event in both photomultiplier tubes is remote due to the coincidence circuitry.

16.3.3.5   Quenching

Quenching is discussed in detail in Section 15.4.5.4. Chemical quenching reduces the amount of energy transferred to the fluor molecules. Halogens, water, solvents, some acids, and oxygen are common agents that cause a decrease in the counting efficiency.

Color quenching is caused by impurities not removed during test-source preparation or by carrier compounds such as iron chloride. Photons emitted from the fluor molecules are absorbed, reducing the amount of light reaching the photomultiplier tubes.

Quenching causes a shift in the scintillation spectrum to lower energies and a reduction in the number of counts. Quenching has a minimal impact on alpha counting, but significantly increases as the energy of the beta particle decreases.

The most common method for monitoring sample quench is through the analysis of a Compton spectrum generated by gamma rays interacting with the sample-scintillation cocktail. 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.

16.3.3.6   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.

16.3.3.7   Test-Source Vials

Glass test-source vials contain naturally occurring impurities such as ^{40}K, Th, and U. 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.

16.3.3.8   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), having a similar quench factor as the test sources, normally is counted with each counting batch and the output will provide the count rate of the blank to be subtracted from each test source.

The detecting 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 detector efficiency[4]. If the internal (standards addition) method is used, the data generated by the counter must be further manipulated in order to develop the counting efficiencies for each test source. When using the external-standards method (quench curve), the scintillation spectrometer will apply the quench corrected efficiency and give the test sample disintegration rate by applying the corrected efficiency.

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[4] For a discussion of liquid scintillation efficiency determination, see Section 15.5.3.

The radionuclide or gross concentration is provided by the following equation:

$$A_C = \frac{C_G - C_B}{\varepsilon_q V}$$

(16.22)

where:

C_G = gross counting rate (source + background) (cps)
C_B = counting rate of the blank (cps)
ε_q = radionuclide quench-corrected counting efficiency for the specific radionuclide (cps or Bq)
A_C = radionuclide or gross concentration (Bq/L or Bq/g)
V = volume or mass analyzed (L or g)

16.4   Data Reduction on Non-Spectrometry Systems

Proportional counters are primarily used for counting of test sources for alpha and beta emitters. Proportional counters may have entry windows for allowance of the emitted radiation into the active portion of the detector or they may be windowless. These instruments are described in Chapter 15. They are used for the determination of specific radionuclides, following chemical separation to isolate the radionuclide, and for nonspecific (gross) analyses. Counters are equipped to count alpha and beta simultaneously in a given source and report the activity of both.

The basic information obtained from a determination in a proportional counter is the number of counts recorded in the detector within the allotted counting duration. However, modern proportional counters take the data reduction process to the point of finality, i.e., producing the test-source concentration and associated counting uncertainty, providing automatic instrument background subtraction, and correcting for source self-absorption and alpha/beta crosstalk.

The instruments may also have protocols for developing the correction factors for self-absorption and for crosstalk. In addition, they should have the capacity to track and evaluate the periodic QC checks (check source and background) performed on the instrument.

The basic equation used to calculate test-source activity is:

$$A = \frac{C_G - C_B}{\varepsilon}$$

(16.23)

where:
A = the activity of the radionuclide or gross activity (Bq)
C_G = the gross counting rate (source + background) (cps)

C_B = the instrument background counting rate (cps)
ε = the gross or radionuclide counting efficiency (cps or Bq)

And the radionuclide or gross concentration is provided by the following equation:

$$A_C = \frac{C_G - C_B}{\varepsilon V} \qquad (16.24)$$

where:

A_C = radionuclide or gross concentration (Bq/L or Bq/g)
V = the volume or mass analyzed (L or g)

The associated combined standard uncertainty is given by:

$$u_c(A_C) = \sqrt{\frac{u^2(C_G) + u^2(C_B)}{\varepsilon^2 V^2} + A_C^2 \left(\frac{u^2(\varepsilon)}{\varepsilon^2} + \frac{u^2(V)}{V^2} \right)} \qquad (16.25)$$

The above simple equations apply to counting either pure alpha or beta emitters and when no correction for self-absorption is necessary (weightless sources). Modifications should be made in the activity and concentration calculations when both alpha and beta particles are emitted by the source, and when absorption and scattering within the source cause a reduction in the effective efficiency.

Self-absorption factors are applied for sources where the self-absorption of the alpha or beta particle is sufficient to affect the overall efficiency (Chapter 15). 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 15). 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

$$\varepsilon_m = a_0 + a_1 m + a_2 m^2 + a_3 m^3 \qquad (16.26)$$

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

$$u_c(\varepsilon_m) = \sqrt{u^2(a_0) + \sum_{i=1}^{3} m^{2i} u^2(a_i) + 2\sum_{i=0}^{2}\sum_{j=i+1}^{3} m^{i+j} u(a_i, a_j) + (a_1 + 2a_2 m + 3a_3 m^2)^2 u^2(m)} \quad (16.27)$$

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

$$\varepsilon_m = \varepsilon_{zero} e^{-am} \quad (16.28)$$

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:

$$u_c(\varepsilon_m) = e^{-am}\sqrt{a^2 u^2(m) + u^2(\varepsilon_{zero}) + m^2 u^2(a) - 2m\, u(\varepsilon_{zero}, a)} \quad (16.29)$$

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 that 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 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:

$$X_\alpha = \frac{\beta}{\alpha + \beta} \qquad (16.30)$$

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:

$$X_\beta = \frac{\alpha}{\alpha + \beta} \qquad (16.31)$$

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:

$$\alpha = \alpha_d - \alpha_d X_\alpha + \beta_d X_\beta \qquad (16.32)$$

$$\beta = \beta_d - \beta_d X_\beta + \alpha_d X_\alpha \qquad (16.33)$$

Equation 16.32 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 16.33 is the equivalent of Equation 16.32 for beta counts. Solving the equations simultaneously for α_d and β_d gives:

$$\alpha_d = \frac{\alpha - X_\beta(\alpha + \beta)}{1 - X_\alpha - X_\beta} \qquad (16.34)$$

$$\beta_d = \frac{\beta - X_\alpha(\alpha + \beta)}{1 - X_\alpha - X_\beta} \qquad (16.35)$$

Their associated combined standard uncertainties are:

$$u_c(\alpha_d) = \frac{\sqrt{u^2(X_\alpha)\alpha_d^2 + u^2(X_\beta)(\alpha_d - \alpha - \beta)^2 + u^2(\alpha)(1 - X_\beta)^2 + u^2(\beta)X_\beta^2}}{1 - X_\alpha - X_\beta} \qquad (16.36)$$

$$u_c(\beta_d) = \frac{\sqrt{u^2(X_\beta)\beta_d^2 + u^2(X_\alpha)(\beta_d - \alpha - \beta)^2 + u^2(\beta)(1 - X_\alpha)^2 + u^2(\alpha)X_\alpha^2}}{1 - X_\alpha - X_\beta} \qquad (16.37)$$

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 that 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 that may be performed for scintillation detectors, ionization chambers, and special instruments include the following:

• Determining background and subtraction;
• Converting total counts to counts per second;
• Calculating activity using calibration data;
• Calculating concentration using activity and operator input data;
• Performing efficiency calibrations;
• Calculating counting and total uncertainty;
• Determining crosstalk and corrections;
• Determining self-absorption corrections;
• Determining radioactive decay corrections; and
• Performing 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.

16.5 Internal Review of Data by Laboratory Personnel

The final review of analytical data by the laboratory should be according to the laboratory quality manual or other documented procedures to ensure that the data meets specified requirements. All final inspections and reviews of data should be performed, documented and archived. The review of analytical data may be performed on two levels: primary and secondary. Different people should perform these two levels. Primary and secondary reviewers should be designated by management.

16.5.1 Primary Review

Some elements to consider in the primary review are:

- Verifying that all tests requested were performed for all samples
  - Target radionuclides
  - Sample preservation
  - Required sample preparation (filtration of liquid samples, drying of soils, etc.
- Comparing the actual sample (radiological) holding times to the holding times specified in the analytical methods; holding-time exceedences should be documented in the final report
- Verifying that the appropriate method was selected and performed
- Determining that the target radionuclides were correctly identified
- Verifying that data inputs for calculations were correct
  - Examining the calibration curve to determine that the criteria specified in the analytical method were met (or verifying radiotracer activity used)
  - Dates and times for reference/sample, analysis, ingrowth/decay, chemical separation
  - Sample volumes/mass, detector backgrounds or analytical blanks, radionuclide half life, etc.
- Checking for errors in transcription and data inputs for calculations (such as rounding procedures and correction factors)
- Checking, by independent hand calculations when possible and at a specified frequency, automated data results for correct quantification
- Reviewing measurements results for reasonableness
- Verifying that measurement results meet MQO requirements
- Examining QC sample results for acceptable performance
- Verifying that the analyst's notebook and/or project file—
  - accurately captures the final results
  - is readable
  - documents any deviations from the analytical method
  - contains the analyst's initials or signature (written or electronic) and the completion date of the analyses

16.5.2 Secondary Review

The secondary review includes many of the same considerations as the primary review; however, there are additional aspects that may be addressed:

- Verifying that a primary review has been conducted
- Verifying that the correct analytical method was performed
- Verifying that the correct software was used to calculate the measurement results
- Examining computerized printouts for completeness
- Examining the final results, including QC sample results to determine if all relevant data

have been included
• Preparing or reviewing the Case Narrative to be included in the data package
• Verifying that all required signatures are included

16.6 Reporting Results

Quality planning documents will give the level of data reporting required. This level will vary from simply reporting the analytical results 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 recommends that the reported value of a measurement result: (1) be reported directly as obtained, with appropriate units, even if it is are negative, (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 combined standard uncertainty (ANSI N42.23) or the expanded uncertainty.

16.6.1 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 N42.23). Other information that 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.

16.6.2 Units and Radionuclide Identification

The individual radionuclides should be identified or, for gross analyses, the category, e.g., gross alpha/beta, should be reported. For gross alpha and beta measurements, it is common practice to cite the "reference" radionuclide used to calibrate the detector or generate the detector efficiency factors from self absorption curves (e.g., ^{137}Cs for gross beta analyses). In some cases, the reference radionuclide will be specified by the project manager. The citation to the reference radionuclide should be made on the analytical reports submitted by the laboratory.

Reporting units are likely specified by project planning documents. If not specified, when

possible, the International System of Units (SI) is 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 16.1 for common matrices.

TABLE **16.1 — 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 g^{-1}	Bq g^{-1}	37
Surfaces	dpm/100 cm^2	Bq/100 cm^2	1.67×10^{-2}

16.6.3 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. MARLAP recommends that the measurement uncertainty be rounded to two significant figures, and that both the value and uncertainty be reported to the resulting number of decimal places (see Sections 19.3.7 and 19.3.9). 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 minimum detectable concentration (MDC) should be reported to two significant figures (ISO, 1995; ANSI N42.23). It should be noted that rounding should only occur in reporting the final results.

16.7 Data Reporting Packages

Project planning documents (Chapter 4) and analytical statements of work (Chapter 7, *Evaluating Methods and Laboratories*) usually define the requirements of the final data submission. The reporting of laboratory data may vary according to laboratory, SOW, or data validation require-ments. If the laboratory has been requested to report the results for several radionuclides (as many as 20 in some applications) for each sample ID, the results for the required radionuclides may be reported together on a single report form. (An exception to this is the reporting of results from gamma-ray analyses.) Many projects will specify a data package of reports and supporting information necessary to describe, document, and define the analytical process. Table 16.2 provides a fairly comprehensive list of elements that might be included in a radiochemical data package, although not all will be applicable to a single data package and some are only applicable during an audit.

TABLE 16.2 — **Example elements of a radiochemistry data package**

General Information	

• Table of contents (especially for large packages)
• Laboratory name
• Client name
• Identification of project, SOW, etc.
• Identification of the sample batch
• A complete list of samples, including:
  – Client sample ID
  – Laboratory sample ID
  – Sample matrix
  – Collection date(s)
  – Date of receipt by laboratory
• Verification of field sample preservation
• Signed acknowledgment of data package completeness
	Supporting laboratory documentation, such as copies of:
	• Relevant logbook pages
	• Standard certificates
	• Bench sheets
	• Instrument printouts, spectrum graphs
	• Control charts and QC reports (including instrument QC)

Batch-Specific Information
• Unambiguous identification of the sample preparation and analytical procedures • Narrative describing how samples were received and processed • Notes of problems encountered (e.g., shipping problems, QC failures, deviations from the SOW or SOPs) • Explanations of terms, acronyms, other aspects of the report that may be unclear to the client • Identification of all preparation batches • Identification of analyst(s), either by batch or by sample • QC linkages (which QC samples go with which samples)

Analysis-Specific Information (For each test performed on an actual sample or QC sample)
• Laboratory sample ID • Preparation batch ID • Size of sample aliquant • Which portion or fraction of sample was tested (if applicable; e.g., filtrate, undissolved solids) • Chemical yield (if appropriate), with uncertainty

For Each Instrumental Analysis	For Each Analyte Measured
• Instrument ID • Type and description • Date of most recent calibration • Duration of analysis • Description of test-source geometry	• Analyte identifier • Measured result • Measurement unit • Uncertainty (with coverage factor) • Critical value • Minimum detectable concentration • Reference dates and times (for decay and ingrowth corrections)

QC-Sample Information	Chain-of-Custody Information
• Type of QC sample (matrix spike, etc.) • Numerical value of performance indicator • Pass-or-fail evaluation	• Chain-of-custody or other tracking documents provided with samples or generated by the laboratory identifying the dates and times of the sample history

16.8   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 transferred directly into a project database or, in some cases, into validation/review programs, and avoids transcription errors. Many of the elements in Table 16.2 may be reported electronically, but the record structure may vary in terms of database compatibility, field length, field order, and field name. Because there is no universal structure for EDDs, the laboratory may be required to produce them in various formats.

EDDs may be transmitted by direct electronic transfer, e-mail, or on removable media (disks, tapes, cartridges, CD-ROMs, removable hard drives). More information may be found at the following websites:

• The U.S. Department of Energy's Environmental Management Electronic Data Deliverable (EMEDD) may be found at ersmo.inel.gov/edd/.

• The U.S. Environmental Protection Agency's Environmental Data Registry is available at www.epa.gov/edr/.

• The U.S. Air Force Environmental Resources Program Management System (ERPRIMS) website (www.afcee.brooks.af.mil/ms/msc_irp.asp) also provides useful information on environmental databases and EDDs.

One EDD that promises to become a widely adopted format is the Staged Electronic Data Deliverable (SEDD) being developed jointly by the U.S. Army Corps of Engineers and the U.S. Environmental Protection Agency. SEDD is based on XML (eXtensible Mark-up Language) technology, which is a World Wide Web Consortium (www.w3.org) standard. SEDD will be adaptable for use with any agency or program database format through the use of parsers that transfer data from SEDD to the appropriate database elements. With the widespread adoption of SEDD, laboratories should need to produce only one type of EDD. Information on SEDD can be found at www.epa.gov/superfund/programs/clp/sedd.htm.

16.9   References

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17 WASTE MANAGEMENT IN A RADIOANALYTICAL LABORATORY

17.1 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. While MARLAP otherwise is consistent in using SI units, this chapter uses whichever units are in the referenced regulations. Sections 17.2 through 17.5 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 17.2. Section 17.3 reviews various approaches that have been used to achieve effective laboratory-waste management programs. Waste minimization programs are discussed in Section 17.4. Waste characterization is reviewed briefly in Section 17.5. Some of the specific regulatory requirements that apply to laboratory waste management are provided in Section 17.6. A proposed outline for a waste management plan is provided in Section 17.7, and Section 17.8 suggests a number of useful online resources related to the management of laboratory waste.

17.2 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, while a multiservice laboratory that performs a variety of processes may produce many waste streams. Waste streams produced by radio-analytical procedures can include radioactive and nonradioactive wastes. A laboratory waste stream is defined as all wastes that are produced by a given analytical process. Table

Contents

17.1 provides a list of wastes that may be generated by a laboratory.

TABLE 17.1 — 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
Organic solvent waste (used solvents, analytical processes)	Used solvents, degreasers 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, bloodborne 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 biphenyls (PCB), asbestos, chlorinated dioxins/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 radioactive wastes and RCRA or TSCA wastes

17.3   Waste Management Program

EPA (1996) provides useful guidance for the laboratory to develop a waste management plan. This report reviews various approaches that have been taken to achieve effective laboratory waste-management programs. It reviews a number of articles and books that detail the experiences of laboratories that manage radioactive wastes. This section draws significantly from that report.

17.3.1 Program Integration

Successful waste management programs integrate important components, such as administration, 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.

17.3.2 Staff Involvement

All levels of management, scientists, and technicians should be involved actively in developing and implementing the waste management program, because each brings a valuable and unique perspective to the waste management issue. Senior 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 provide perspective on such issues 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, because they typically interface with regulators to ensure that waste management practices are fully compliant. Input from laboratory supervisors, scientists, and technicians is necessary because they generate waste at the bench level and have firsthand 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. U.S. Department of Energy (DOE) Order 435.1 endorses the concept of waste life-cycle management to reduce the amount of radioactive waste generated. "Waste life cycle" is 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.

17.4 Waste Minimization

Minimizing waste 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" is an 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 minimization may result in the most substantial cost savings. Two important 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 17.1. 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 generation, 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 nonradioactive 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 nonradioactive, 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, because waste considered nonradioactive in one state may be considered radioactive in another.

Once the waste has been properly categorized (e.g., 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 nonradioactive 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 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 nonhazardous 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 advance 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 microscale 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 nonhazardous substitute is available. Rotating chemical stock (first in, first out) may help avoid expiration of the chemical shelf life.

REUSE OF MATERIALS. Some materials may be recovered from the analytical process and reused in subsequent analyses. For example, distillation of certain used organic solvents may purify them sufficiently for reuse.

DECAY IN STORAGE. Because 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 nonradioactive 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:

- Nonhazardous waste mixed with hazardous waste must be managed as hazardous waste.
- Nonradioactive 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.

17.5 Waste Characterization

Laboratory wastes should be characterized properly to assure compliance with applicable federal, state, and local regulations, and to determine appropriate means of disposal. Waste container contents should be characterized adequately 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 (e.g., 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 characterize waste correctly .

A generic laboratory waste management plan should be established to describe the waste life cycle. This plan should characterize each waste stream and establish a waste-stream profile, so that the waste stream can be managed properly. The profiled waste stream may only require a periodic partial characterization, based on the profile and regulatory status.

17.6 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, because waste management requirements can be complex and contradictory.

Radioactive waste is regulated under AEA, administered by the Nuclear Regulatory Commission

(NRC). Thirty-two states are NRC Agreement States (www.hsrd.ornl.gov/nrc/) 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 difficult due to the complex regulatory framework and the lack of approved treatment and disposal options for these wastes (also see "Mixed Waste Exemption" within Section 17.6.1). Other laws, such as the Clean Water Act and the Clean Air Act, 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 Titles 10 and 40 of the *Code of Federal Regulations*. The following 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). 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 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 apply to an analytical laboratory relate to PCB wastes. Laboratory wastes 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.

17.6.1 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. Regulations issued in 2001 increased the flexibility of facilities to manage low-level mixed waste (LLMW) by reducing the dual regulation of LLMW under both RCRA and AEA (EPA, 2001). LLMW is exempted from RCRA requirements during storage, treatment, manifest, transportation, and disposal requirements when certain specified conditions are met. Under this conditional exemption, the waste remains subject to manifest, transport, and disposal requirements under NRC (or NRC Agreement States) for low-level radioactive waste. These exemptions, which only apply to certain wastes, do not apply to DOE facilities.

17.6.2 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 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 (LLRW) 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. LLRW 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).

17.6.2.1 Container Requirements

RADIOACTIVE WASTE. NRC has container requirements for LLRW. 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. These requirements may not apply to radioanalytical laboratories processing low-level radioactive samples.

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 nonliquid 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.

17.6.2.2 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).

17.6.2.3 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 exceeds 100 kg, 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.

17.6.2.4 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 radioactivity 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)].

17.6.3 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. 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 nonradioactive waste or in accordance with license conditions.

• Supernates may be disposed in a sewage system, but the pH must be above 2 and 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.

17.6.4 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 concentrations of 0.05 µCi/g 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 µCi/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.

17.7 Contents of a Laboratory Waste Management Plan/Certification Plan

17.7.1 Laboratory Waste Management Plan

A laboratory waste management plan describes the waste generated by the analytical laboratory. Each section of the plan is usually divided into two parts—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 might be:

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.

17.7.2 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. LLRW shall be certified as meeting waste acceptance requirements before it is transferred to the facility receiving the waste.

MAINTAINING CERTIFICATION. LLRW 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 should include:

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 certification (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.

17.8 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
   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.
   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).
   www.epa.gov/fedrgstr/

State and Federal Agency Contact List for Mixed Waste Regulations
   www.epa.gov/rpdweb00/mixed-waste/mw_pg6e.htm

States and Territories Where EPA Regulates Mixed Waste
   www.epa.gov/rpdweb00/mixed-waste/mw_pg6a.htm

States and Territories With EPA Authorization to Regulate Mixed Waste
   www.epa.gov/rpdweb00/mixed-waste/mw_pg6b.htm

State Solid and Hazardous Waste Web Sites
    www.epa.gov/epaoswer/osw/stateweb.htm

RCRA State Authorization, By State and Program Element
    www.epa.gov/epaoswer/hazwaste/state/index.htm

NRC Agreement States
    www.hsrd.ornl.gov/nrc/

DOE Mixed Waste Policies
    www.directives.doe.gov/

EPA Mixed Waste Home Page
    www.epa.gov/rpdweb00/mixed-waste/index.html

Mixed Waste Glossary
    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
    www.epa.gov/rpdweb00/mixed-waste/mw_pg25.htm

Current Mixed Waste Treatment, Storage, or Disposal Facilities (TSDFs)
    www.epa.gov/rpdweb00/mixed-waste/mw_pg11a.htm

NRC/EPA Draft Storage Guidance
    www.epa.gov/radiation/mixed-waste/mw_pg27.htm

Mixed Waste Shipping and Transportation
    www.epa.gov/rpdweb00/mixed-waste/mw_pg10.htm

Mixed Waste Pollution Prevention
    www.epa.gov/rpdweb00/mixed-waste/mw_pg23.htm

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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 and 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

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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 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 *constitutional hetero-geneity* 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 *distributional heterogeneity* of a lot depends not only on the variations among particles but also on their spatial distribution.[1] Thus, the distributional heterogeneity may change, for example, when the material is shaken or mixed. In Gy's theory, both constitution heterogeneity and distributional heterogeneity are quantitative terms, which are defined mathe-matically.

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 distrib-uted, 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 ana-lyte concentration of the sample to the analyte concentration of the lot. A sample is representative if its analyte concentration is close to the analyte 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.

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 characterized as those associated with (sub)sampling and those associated with sample preparation and analysis.

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[1] ASTM D5956 uses the terms "compositional heterogeneity" and "distributional heterogeneity."

[2] A state of random heterogeneity exists when the distributional heterogeneity is zero. A state of nonrandom hetero-geneity exists when the distributional 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.

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:

- 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 Uncertainty*, for a more general discussion of laboratory measurement errors.)

F.3.1 Sampling Bias

Sampling bias is often related to distributional 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 anthropogenic radionuclides are often concentrated in some of 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 mass) than the largest particle of the lot.

RULE 2: The sample must be many times larger (by mass) 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. For this reason, it is usually necessary to do some preparation of the material before sampling. Typical preparation steps in the laboratory include drying, grinding, sieving, and mixing, as described in Chapter 12.

F.3.2 Fundamental Error

When a sample is taken, the existence of constitutional 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 or
- Reducing the particle sizes (grinding) 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 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

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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 $E(\cdot)$ denotes expected value. Equal selection probabilities guarantee only that $E(Z_S) / E(m_S) = z_L$.

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 (see Section 12.3.1.4, "Subsampling")

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 distributional heterogeneity.

The existence of distributional 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.

Some homogenization of solid material is usually required before sampling to reduce clumping. However, since complete homogenization is difficult and likely to be short-lived at best, Gy and Pitard recommend sampling procedures to reduce not the distributional 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-gram sample is required, it is better to take five 5-gram increments, selected from different locations in the sample, than to take a single 25-gram increment.

RULE 5: A sample composed of many increments taken from different locations in the lot is usually more representative than a sample composed of a single increment.

The variance reduction achievable by increment sampling depends on the distributional heterogeneity of the lot. If the lot is in a state of pure random heterogeneity, increment sampling provides no benefit. On the other hand, if the lot is highly stratified, the standard deviation of the analyte concentration of a small composite sample formed from n independent increments may be smaller by a factor of $1/\sqrt{n}$ than the standard deviation for a sample composed of a single increment.[5] Variance reductions intermediate between these two extremes are most likely in practice.

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[5] This statement assumes the stratification is such that a single large increment is likely to have no more constitutional heterogeneity than any of the n smaller increment.

Figures F.1 and F.2 illustrate what Gy calls "increment delimitation error" and "increment extraction error," respectively. One method for extracting increments is the one-dimensional "Japanese slab-cake" method (Gy, 1992; Pitard, 1993). First, the material in the lot is spread out into an elongated pile with roughly constant width and height. Then a scoop or spatula is used to delimit and extract evenly spaced cross-sections from the pile. A flat-bottomed scoop should be used for this purpose to avoid leaving particles at the bottom of the pile. Ideally it should also have vertical sides, as shown in Figure F.3, although such scoops may not be commercially available. If a spatula is used, its width must be much larger than the largest particles to be sampled, since particles will tend to fall off the edges (Figure F.2).
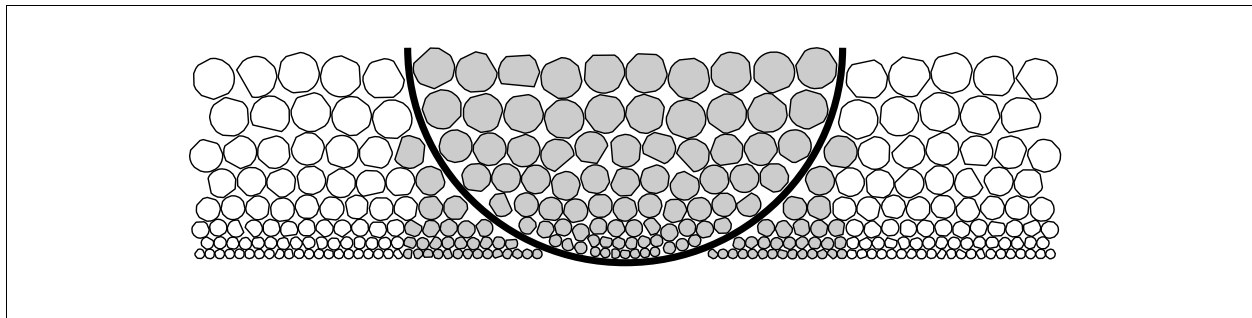

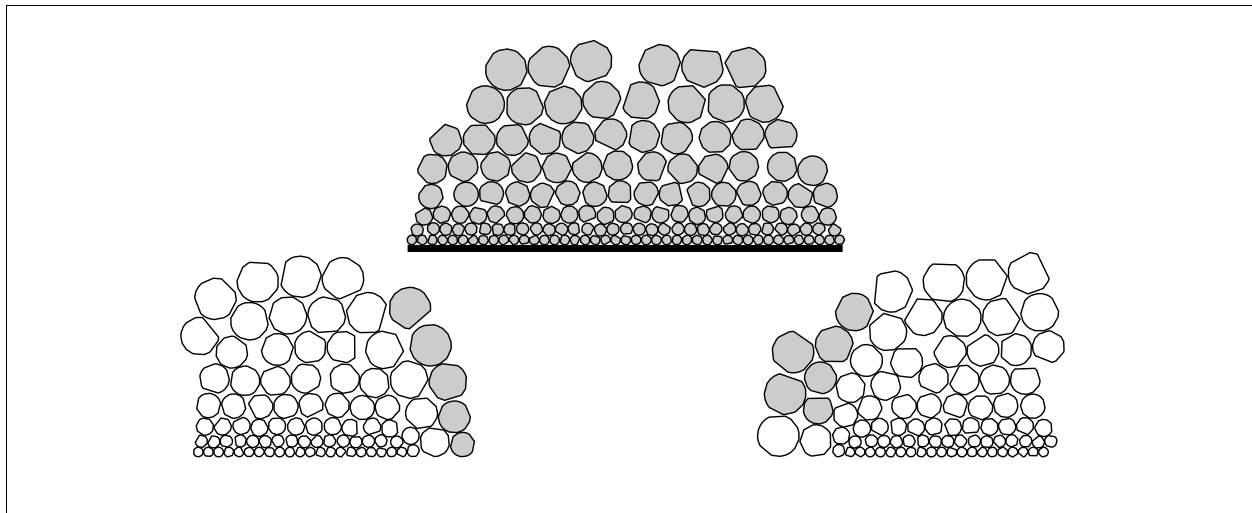**FIGURE F.1 — Incorrect increment delimitation using a round scoop**

FIGURE F.2 — Incorrect increment extraction using a spatula

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.
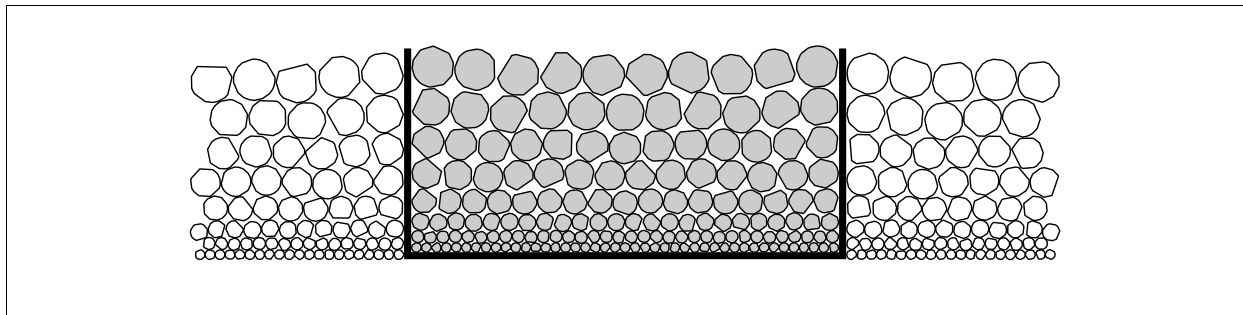

FIGURE F.3 — Correct increment delimitation using a rectangular scoop

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).

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 rough estimates of the uncertainty due to subsampling and as a guide to the factors that are important in subsampling and how their impact on the uncertainty might be mitigated.

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):

$$\sigma^2_{FE} = \left(\frac{1}{m_S} - \frac{1}{m_L} \right) \sum_{i=1}^{N} \frac{(z_i - z_L)^2}{z_L^2} \frac{m_i^2}{m_L} \tag{F.1}$$

Here

m_S is the mass of the sample;
m_L is the mass of the lot;
N is the number of particles in the lot;
z_i is the analyte concentration of the ith particle;
z_L is the analyte concentration of the lot; and
m_i is the mass of the ith particle.

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 anthropogenic 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 nonnatural

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

$$\sigma_{FE} = \sqrt{\left(\frac{1}{m_S} - \frac{1}{m_L}\right) kd^3} \tag{F.2}$$

where the value of the coefficient k depends on the characteristics of the material.[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 percent 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

$$\sigma_{FE} = \sqrt{\frac{kd^3}{m_S}} \tag{F.3}$$

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 anthropogenic 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:

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[6] Gy (1992) and Pitard (1993) provide more information about the coefficient 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.

- 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.

Under these assumptions the fundamental standard deviation σ_{FE} is described by the equation[8]

$$\sigma_{FE} = k \sqrt{\left(\frac{1}{m_S} - \frac{1}{m_L}\right) \frac{z_{max}\,\varrho_H\,d_H^3}{2\,z_L}} \tag{F.4}$$

where

m_S is the sample mass;
m_L is the mass of the lot;
ϱ_H is the average density of a high-activity particle;
d_H is the maximum diameter of a high-activity particle, defined as in Scenario 1; and
k is a dimensionless factor.

The value of the factor k depends on the distribution of sizes of the high-activity particles but is most likely to lie between 0.5 and 1.[9]

When m_S is much smaller than m_L, Equation F.4 reduces to

$$\sigma_{FE} = k \sqrt{\frac{z_{max}\,\varrho_H\,d_H^3}{2\,z_L\,m_S}} \tag{F.5}$$

If all the high-activity particles have approximately the same mass and the sample mass is much smaller than the mass of the lot, then Equation F.5 may be rewritten in the simple form

$$\sigma_{FE} \approx \sqrt{\frac{m_L}{m_S\,n_L}} \tag{F.6}$$

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[8] A more complete formula is $\sigma_{FE} = \left[\left(\frac{1}{m_S} - \frac{1}{m_L}\right) \frac{z_{max} - z_L}{2\,z_{max}} \left(\frac{z_{max} - z_L}{z_L}\,\varrho_H k_H^2 d_H^3 + \varrho_G k_G^2 d_G^3\right)\right]^{1/2}$, where ϱ_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 factor 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 numerically equal (Chapter 19, *Measurement Uncertainty*). The fundamental standard deviation equals the coefficient of variation of the Poisson distribution, which is large when the mean is small.

EXAMPLE F.1

A 1-kilogram lot of soil contains approximately 1 Bq/g of ^{240}Pu occurring as hot particles of relatively pure plutonium dioxide (^{240}PuO$_2$, density $\varrho_H = 11.4$ 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,

$$\sigma_{FE} = 0.5\sqrt{\frac{(7.44 \times 10^9 \text{ Bq/g})(11.4 \text{ g/cm}^3)(10^{-3} \text{ cm})^3}{2 \times (1 \text{ Bq/g}) \times (1 \text{ g})}} \approx 3.3$$

Thus, the fundamental standard deviation is about 330 percent, indicating that a 1-gram 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 percent.

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 (e.g., colloidal particles or 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

$$\sigma_{FE} = k \sqrt{\left(\frac{1}{m_S} - \frac{1}{m_L}\right) \frac{\varrho d^3}{2}}$$

(F.7)

where
$\qquad m_S$ is the sample mass;
$\qquad m_L$ is the mass of the lot;
$\qquad \varrho$ is the average particle density;
$\qquad d$ is the "maximum" particle diameter, as defined for Scenario 1; and
$\qquad k$ is a dimensionless factor.

The value of 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

$$\sigma_{FE} = k \sqrt{\frac{\varrho d^3}{2 m_S}}$$

(F.8)

The fundamental standard deviation σ_{FE} calculated using Equation F.8 is never greater than $\sqrt{\varrho d^3 / 2 m_S}$, which is the square root of the ratio of the "maximum" particle mass $\varrho d^3 / 2$ 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 assumptions underlying Equation F.8 to be violated if the contaminant is not redistributed onto the newly created particle surfaces.

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[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.

EXAMPLE F.2

Suppose a 1-kilogram 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-gram sample?

Assuming the density of the soil particles is $\varrho = 2.675$ g/cm^3, Equation F.8 with $k = 1$ gives the solution

$$\sigma_{FE} = \sqrt{\frac{(2.675 \text{ g/cm}^3)(0.2 \text{ cm})^3}{2 \times (1 \text{ g})}} = 0.10 \text{ or } 10 \text{ percent.}$$

Note that since k is usually less than 0.5, the fundamental standard deviation is more likely to be less than 5 percent.

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 (e.g., by drying and sieving).

- 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 (grinding) 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 tools and procedures that ensure each particle in the lot has the same probability of selection. Any sampling tool or procedure that prefers certain particles (e.g., because of their density, size, or shape) may produce a sampling bias.

• 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.

F.6   References

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