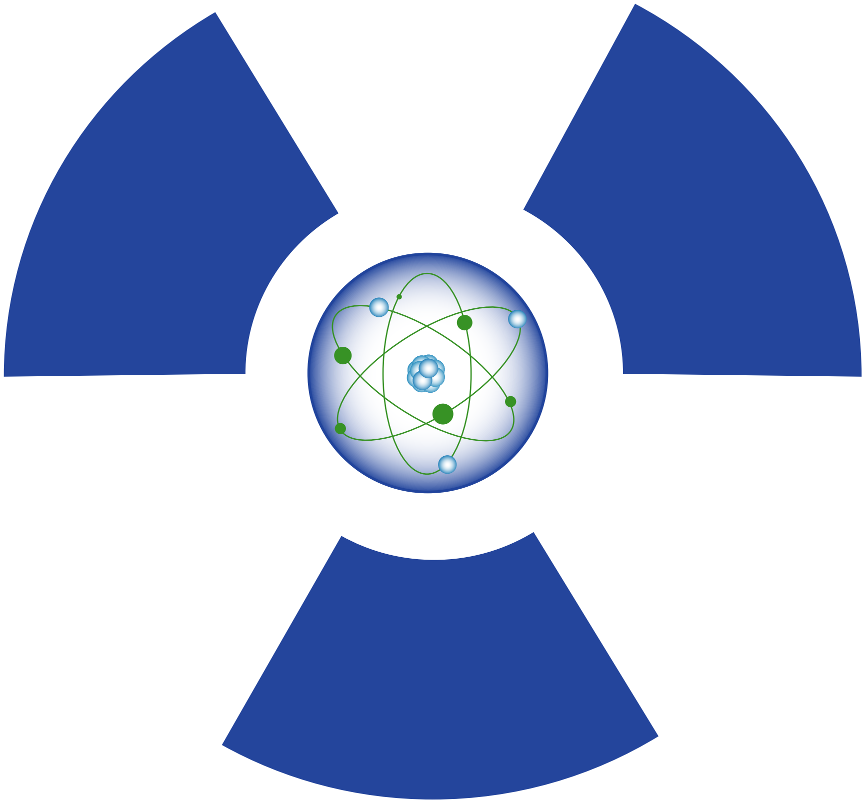
UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

Inventory of Radiological Methodologies

For Sites Contaminated with Radioactive Materials



EPA 402-R-06-007
www.epa.gov
October 2006

Inventory of Radiological Methodologies

For Sites Contaminated With Radioactive Materials

U.S. Environmental Protection Agency
Office of Air and Radiation
Office of Radiation and Indoor Air
National Air and Radiation Environmental Laboratory
Montgomery, AL 36115

This report was prepared for the National Air and Radiation Environmental Laboratory of the Office of Radiation and Indoor Air, United States Environmental Protection Agency. It was prepared by Environmental Management Support, Inc., of Silver Spring, Maryland, under contract 68-W-00-084, work assignment 46, and contract 68-W-03-038, work assignments 10 and 26, all managed by David Garman. Mention of trade names or specific applications does not imply endorsement or acceptance by EPA. For further information, contact Dr. John Griggs, U.S. EPA, Office of Radiation and Indoor Air, National Air and Radiation Environmental Laboratory, 540 South Morris Avenue, Montgomery, AL 36115-2601.

Preface

This compendium is part of a continuing effort by the Office of Radiation and Indoor Air and the Office of Superfund Remediation and Technology Innovation to provide guidance to engineers and scientists responsible for managing the cleanup of sites contaminated with radioactive materials.

The document focuses on the radionuclides likely to be found in soil and water at cleanup sites contaminated with radioactive materials. However, its general principles apply also to other media that require analysis to support cleanup activities. It is not a complete catalog of analytical methodologies, but rather is intended to assist project managers in understanding the concepts, requirements, practices, and limitations of radioanalytical laboratory analyses of environmental samples.

As with any technical endeavor, actual radioanalytical projects may require particular methods or techniques to meet specific analytical protocol specifications and data quality objectives.

Detailed guidance on recommended radioanalytical practices may be found in current editions of the *Multi-Agency Radiological Laboratory Analytical Protocols Manual* (MARLAP) and the *Multi-Agency Radiation Survey and Site Investigation Manual* (MARSSIM), both referenced in this document.

Comments on this document, or suggestions for future editions, should be addressed to:

Dr. John Griggs
U.S. Environmental Protection Agency
Office of Radiation and Indoor Air
National Air and Radiation Environmental Laboratory
540 South Morris Avenue
Montgomery, AL 36115-2601
(334) 270-3450
griggs.john@epa.gov

Acknowledgments

This manual was developed by the National Air and Radiation Environmental Laboratory (NAREL) of EPA's Office of Radiation and Indoor Air (ORIA) in collaboration with ORIA's Radiation Protection Division's Site Cleanup Center and with support from the Office of Superfund Remediation and Technology Innovation.

Dr. John Griggs served as project lead for this document. Several individuals provided valuable support and input to this document throughout its development. Special acknowledgment and appreciation are extended to Mr. Stuart Walker, Office of Superfund Remediation and Technology Innovation; Mr. Ronald Wilhelm, Office of Radiation and Indoor Air; Ms. Schatzi Fitz-James, Office of Emergency Management, Homeland Security Laboratory Response Center; and Mr. David Garman, Office of Radiation and Indoor Air, NAREL. Numerous individuals both inside and outside of EPA provided peer review of this document, and their suggestions contributed greatly to the quality and consistency of the final document.

Technical support was provided by Dr. N. Jay Bassin, Dr. Robert Litman, Dr. David McCurdy, and Mr. Robert Shannon of Environmental Management Support, Inc.

Contents

List of Figures

List of Tables

Acronyms and Abbreviations

(Excluding chemical symbols and formulas)

A	atomic mass number, sum of protons (Z) and neutrons (N)
AA	atomic absorption
AMS	accelerator mass spectrometry
AMU	atomic mass unit
APS	analytical protocol specification
AS	alpha spectrometry
ASTM	American Society for Testing and Materials
ASV	anodic stripping voltammetry
β^-, β^+	negatively and positively charged beta particles
Bq	becquerel (1 dps)
BWR	boiling water reactor
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (“Superfund”)
CFR	*Code of Federal Regulations*
CIA	United States Central Intelligence Agency
Ci	curie
CsI(Tl)	thallium-activated cesium iodide detector
d	day
DCGL	derived concentration guideline level
DHS	United States Department of Homeland Security
DIL	derived intervention level
DOD	United States Department of Defense
DOE	United States Department of Energy
DQO	data quality objective
dpm	disintegration per minute
dps	disintegration per second
DTPA	diethylenetriamine pentaacetic acid
DU	depleted uranium
e^-	electron
$E_{\beta\max}$	maximum energy of the beta-particle emission
EDTA	ethylenediamine tetraacetate
EPA	United States Environmental Protection Agency
FRMAC	Federal Radiological Monitoring and Assessment Center (DOE)
FTIR	Fourier transform infrared
g	gram
Ge	germanium semiconductor
GP	gas proportional
GPC	gas proportional counting
GS	gamma spectrometry
Gy	gray
h	hour
HPGe	high-purity germanium detector
HTGR	high-temperature gas-cooled reactor
IC	ion chromatography

ICP	inductively coupled plasma
ICP-MS	inductively coupled plasma-mass spectrometric
IDA	isotopic dilution analysis
IND	improvised nuclear device (i.e., a nuclear bomb)
ISE	ion-selective electrode
ISO	International Organization for Standardization
IUPAC	International Union for Pure and Applied Chemistry
keV	thousand electron volts
KPA	kinetic phosphorimetry analysis
LEGe	low-energy germanium
LCS	laboratory control sample
LS	liquid scintillation
LSC	liquid scintillation counter
MARLAP	*Multi-Agency Radiological Laboratory Analytical Protocols Manual*
MARSSIM	*Multi-Agency Radiation Survey and Site Investigation Manual*
mCi	millicurie (10^{-3} Ci)
MCL	maximum contaminant level
MDA	minimum detectable activity (of a radionuclide)
MDC	minimum detectable concentration
MeV	million electron volts
min	minute
MQO	measurement quality objective
MS	mass spectrometry
N	number of neutrons in the nucleus
NaI(Tl)	thallium-activated sodium iodide detector
NCP	National Oil and Hazardous Substances Contingency Plan
ng	nanogram (10^{-9} g)
NORM	naturally occurring radioactive material
NPP	nuclear power plant site decommissioning
NRC	United States Nuclear Regulatory Commission
PAG	protective action guideline
PCB	polychlorinated biphenyl
pCi	picocurie (10^{-12} Ci)
PERALS®	Photon-Electron Rejecting Alpha Liquid Scintillation
PDMS	post-defueling monitored storage
PMT	photomultiplier tube
PWR	pressurized water reactor
QA	quality assurance
QC	quality control
rad	radiation absorbed dose
RDD	radiological dispersal device (i.e., “dirty bomb”)
REGe	reverse-electrode germanium
rem	roentgen equivalent: man
s	second
Sv	sievert
Si	silicon semiconductor
SI	International System of Units
SOW	statement of work

$t_{1/2}$	half-life
TENORM	technologically enhanced, naturally occurring radioactive materials
TIMS	thermal ionization mass spectrometry
UV-VIS	ultraviolet-visible spectrometry
VOC	volatile organic compound
y	year
Z	atomic number: the number of protons in the nucleus

Radiometric Unit Conversions

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)	1.00	Bq	dps	1.00
Bq Bq/kg Bq/m^3 Bq/m^3	Picocuries (pCi) pCi/g pCi/L Bq/L	27.0 2.70×10^{-2} 2.70×10^{-2} 10^{3}	pCi pCi/g pCi/L Bq/L	Bq Bq/kg Bq/m^3 Bq/m^3	3.70×10^{-2} 37.0 37.0 10^{-3}
Microcuries per milliliter (µCi/mL)	pCi/L	10^{9}	pCi/L	µCi/mL	10^{-9}
Disintegrations per minute (dpm)	µCi pCi	4.50×10^{-7} 4.50×10^{-1}	pCi	dpm	2.22
Gallons (gal)	Liters (L)	3.78	Liters	Gallons	0.264
Gray (Gy)	rad	100	rad	Gy	10^{-2}
Roentgen Equivalent Man (rem)	Sievert (Sv)	10^{-2}	Sv	rem	10^{2}

INVENTORY OF RADIOLOGICAL METHODOLOGIES

1 Introduction

This report describes appropriate radioanalytical methodologies used to characterize environmental samples containing radionuclides, including screening methodologies and radionuclide-specific analyses. The document is intended for nonradioanalytical specialists, such as Remedial Project Managers or Site Assessment Managers with backgrounds in geology, engineering, or hydrology. Appendix A contains a glossary of terms used in this document.

This introduction briefly covers the nature and major types of radiation, natural and anthropogenic sources of radionuclides, physical considerations unique to radiochemical analysis (such as half-life), the general ways that different types of radiation may be measured, and an overview of the major techniques (such as spectrometry, gross alpha and beta analysis, liquid scintillation and proportional counting). This section also summarizes the aspects of radionuclides that differentiate their analysis from stable and more common chemical contaminants. A more comprehensive discussion of these topics is found in Appendix B.

Section 2 discusses the application of a long-term cleanup process with respect to radiological methodologies described in this document and their application to the media described herein. It provides the overview perspective of which methodologies would be applied at different stages of a project, and how these support the measurement quality objectives (MQO) for the project. This section puts into perspective how results of initial analyses would be used to provide more detailed decision making regarding subsequent analyses and the methodologies to be used.

Section 3 reviews analytical considerations, such as the source term at representative types of sites (DOE cleanup and naturally occurring radioactive materials waste sites). The section also considers sample preservation and transport, parameters affecting quantification (such as oxidation state of the radionuclide), measurement uncertainty, sample analysis and turnaround time, and measurement quality objectives and performance testing.

Section 4 discusses appropriate analytical methodologies and includes tables indicating their suitability for various environmental requirements, such as environmental media, screening, concentration, typical detection limits, and any advantages or disadvantages to the methodologies for use in mixed-waste situations. The section concludes with information on applicable analytical methods for each radionuclide and their detection limits.

Section 5 provides methodologies and unique radioanalytical issues for 18 selected elements. For each of the elements, a table in Appendix D summarizes the key isotopes of that element, their radioactive emissions, achievable detection levels, and typical sample processing times for the techniques used for analysis. Section 6 is a list of sources and web sites with reference materials that support this document.

1.1 Scope and Purpose

The analysis of environmental samples for radionuclides requires the overlap of many different scientific disciplines. This document provides an overview of how these disciplines mesh during the sampling and analysis process. It does not go into the underlying scientific principles for each of these disciplines but instead provides a summary of information, which will help to guide the user when evaluating the process of radionuclide analysis in environmental samples.

The information presented here represents a small portion of the potential process for the investigation and evaluation of sites that may have become radioactively contaminated. It is important to note that this information can be used at many different stages of a site project in order to select the appropriate methodology for the analysis results required to support the project MQOs.

Figure 1 shows the major steps for processing an environmental sample from receipt by the laboratory to reporting. Each of these steps is described in this document, as well as the effect each can have on final analytical results.

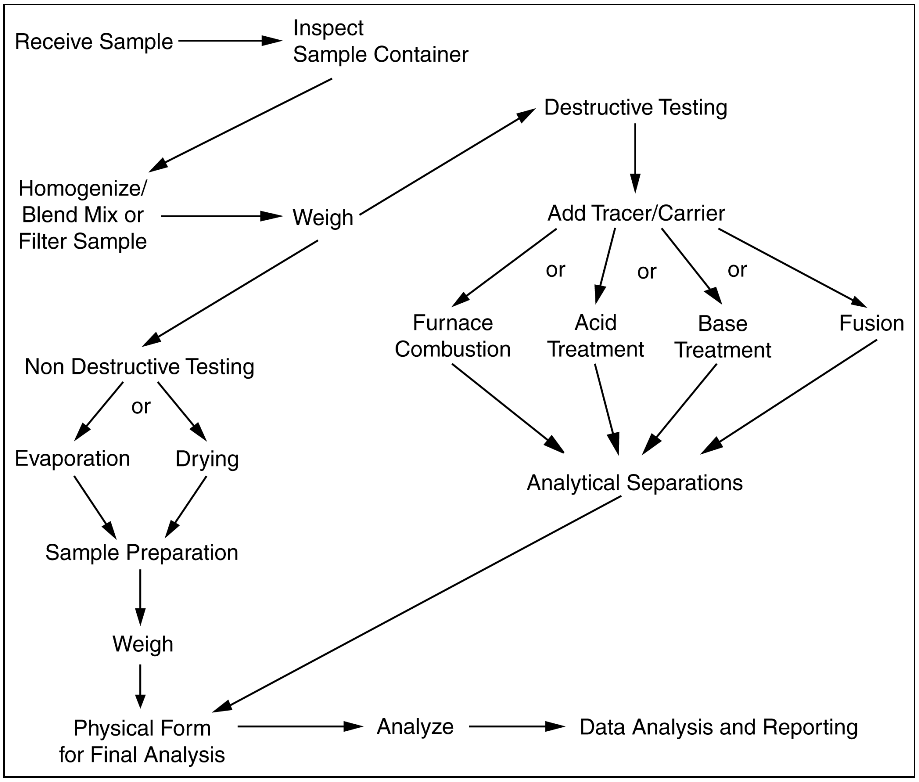


FIGURE 1 — Schematic example of sample process flow

The scope of the document is limited to selected types of sites, samples, radionuclides, and analytical methodologies. This document focuses on water and soil samples[1], and how sampling, sample transport and preservation, and chemical analyses can determine the overall reliability of the

---

[1] Other media, including milk, meat, produce, and forage may require analysis for some site cleanup projects and during responses at a nuclear power plant incident. Radionuclides in these media are analyzed routinely by EPA, and achievable MDC values are available at www.epa.gov/narel/radnet/erdonline.html.

final data. Appendix C identifies characteristics and parameters for radionuclides to be found at these sites. The types of sites that this document addresses are:

- Department of Energy (DOE) site cleanup activities and
- Naturally occurring radioactive materials (NORM) site cleanup activities.

For completeness, some data are provided in the appendices relevant to nuclear power plant decommissioning.

The types of applicable water samples are ground water, surface runoff, and drinking water. This document specifically excludes wastewater, seawater, or any water that has been chemically treated. The three types of water samples addressed in this document have chemical characteristics that are similar. Therefore, no distinction will be made between the way in which they are described in this document for the purposes of radionuclide analysis. However, the water samples that are addressed here may contain hazardous materials or hazardous wastes. For example, ground-water samples at a DOE site may contain radionuclides like ^{137}Cs and ^{3}H and also volatile organic compounds (VOCs) or lead.

The types of applicable soil samples are those expected to be found in a “clean” environment that have been subjected to radioactive contamination. These samples may contain however materials like polychlorinated biphenyls (PCBs) and paint residues. Thus, types of soils specifically excluded are municipal landfill soils, sanitary waste system sludges, soils with significant contamination from organic solvent or solid wastes, or ocean sediment.

The information provided in this document can assist individuals involved in a cleanup process for a radioactively contaminated site. Three tiers of radioanalytical methodologies are presented that may be used during the various phases of a cleanup process, including methodologies for soil screening (EPA, 2000) and the determination of site-specific soil partition coefficients (K_d). Although typical values of soil partition coefficients for radionuclides can be found in published references (EPA, 1999), in many cases it may be desirable to determine a site-specific K_d value for use in computer pathway analysis models in order to obtain a better estimate of the radiation risks for existing or future radionuclide contamination and to determine acceptable remediation limits. In most cases, in order to obtain accurate estimates of a site-specific K_d value for a radionuclide, highly accurate (radionuclide-specific) laboratory radioanalytical methods should be used. It is important that unique analytical protocol specifications be developed for the radioanalytical analyses used for the determination of site-specific K_d values.

1.2 Principles of Radioactivity

A more detailed technical description of radioactivity can be found in Appendix B. The chemistry of an element is determined by the number of protons in its nucleus. Elements are subdivided into nuclides, defined as any species of atom having a specified number of protons and neutrons. For a given number of protons, that element will be stable only if certain number(s) of neutrons are present as well. Two atoms of an element with differing numbers of neutrons are referred to as isotopes. Certain combinations of protons and neutrons lead the nucleus to be unstable and undergo decomposition, known as radioactive decay. A nuclide that undergoes radioactive decay is referred to as a radionuclide. The rate of radioactive decay is specific for each radionuclide and can provide a means for distinguishing one radionuclide from another. The rate of decay is related to the number of total radioactive atoms present at the time of measurement, or

$$A = \lambda N$$

where A is the rate of decay or "activity," measured in atoms decaying per second
λ is the decay constant for the radionuclide in units of sec^{-1} ($\approx 0.693/t_{1/2}$), and
N is the number of atoms present at the time of the measurement.

The following formula identifies how the rate of radioactive decay changes as a function of time for any radionuclide:

$$A = A_0 \, e^{-\lambda t}$$

where A is the rate of decay at the time of measurement
A_0 is the rate of decay at some time before the measurement is made, and
t is the time elapsed between the two activity measurements in the same units as λ.

When the radionuclide undergoes decay, it is seeking to obtain energetic stability. In order to achieve this stability, one or more atomic particles or photons will be emitted. This emission is referred to as "radiation." The basic types of radiation are:

- Alpha
- Beta negative (equivalent to an electron)
- Beta positive (a positron)
- Gamma
- X-rays.

The measurement of the energy, type, and number of these particles or photons emitted (per unit time interval) can be related to the quantity of the radionuclides present in the sample. The traditional radiochemical methods of analysis (such as gas proportional counting, liquid scintillation and gamma-ray analyses) are able to provide specific analytical values for most radionuclides.

Some radionuclides have half-lives and particle energies that make it impossible to distinguish one radionuclide from another with conventional techniques. Examples of these are ^{239}Pu and ^{240}Pu, or ^{243}Cm and ^{244}Cm. Their alpha particle energies are too close to be distinguished by particle counting techniques, and their half-lives are too long to distinguish between the two isotopes by the rate-of-decay evaluation method. Thus they are generally reported as a combined activity, such as "$^{239/240}$Pu = 4.1×10^{-2} pCi/L," signifying that the stated value is the sum of the two radionuclide activities.

In recent years specialized methodologies (such as accelerator mass spectrometry, or inductively coupled plasma-mass spectrometry) have been developed to analyze for such radionuclides individually. These are discussed in sections 2, 3, and 4. These techniques look for total number of atoms present of the radionuclides rather than examining the decay characteristics of the radionuclides.

1.3 Radioactive Decay Chains

Many naturally occurring radionuclides undergo decay to atoms that are also radioactive. The second generation radionuclide (referred to as first progeny) will decay to another atom, which also may be radioactive. For a radionuclide such as ^{238}U, this pattern continues until a stable element is reached. The term used to describe the connection of these radionuclides is "decay chain." The ^{238}U decay chain has 14 progeny participants. This means that typical environmental samples containing ^{238}U will also contain some concentration of all of its progeny as well. The amount of each will depend on the sample history, environmental conditions and the individual chemistry of each progeny and the parent.

1.4 Radionuclides Covered in this Document

The specific radionuclides discussed in this document are listed in Table 1, together with their minimum detection limits and maximum allowable effluent concentrations in water according to federal regulations. Other parameters are listed in Appendices A and B.

TABLE 1 — Radionuclides covered in this manual

Element (Symbol)	Radionuclide/ Isotope (Mass Number)	Minimum Detection Limits[*] pCi/L (mg/L)	Maximum Contaminant Levels in Water[†] pCi/L (mg/L)
Americium (Am)	241	§	15[**] (4.38×10^{-9})
	243	§	15[**] (7.53×10^{-8})
Bismuth (Bi)	210	§	—
Carbon (C)	14	§	2,000 (4.48×10^{-7})
Cesium (Cs)	134	10 (7.7×10^{-12})	80 (6.22×10^{-11})
	137	§	200 (2.31×10^{-9})
Cobalt (Co)	60	§	100 (8.86×10^{-12})
Hydrogen (H)	3	1×10^{3} (1.03×10^{-10})	20,000 (N/A)
Iodine (I)	125	§	—
	129	§	1 (5.68×10^{-6})
	131	1 (8.0×10^{-15})	3 (2.41×10^{-15})
Iridium (Ir)	192	§	100 (2.41×10^{-15})
Lead (Pb)	210	§	—
Nickel (Ni)	59	§	300 (3.77×10^{-6})
	63	§	50 (8.83×10^{-10})
Phosphorus (P)	32	§	30 (1.05×10^{-13})
Plutonium (Pu)	238	§	15[**] (8.87×10^{-10})
	239	§	15[**] (2.42×10^{-7})
	240	§	15[**] (2.76×10^{-10})
	241	§	300 (2.92×10^{-9})
Radium (Ra))	226	1 (1.0×10^{-9}	5[‡] (5.06×10^{-9})
)	228	1 (3.7×10^{-12}	5[‡] (1.8×10^{-11})
Strontium (Sr)	89	10 (3.4×10^{-13})	20 (6.89×10^{-13})
	90	2 (1.4×10^{-11})	8 (5.81×10^{-11})
Sulfur (S)	35	§	500 (inorganic only) (1.17×10^{-11})
Technetium (Tc)	99	§	900 (5.32×10^{-5})
Thorium (Th)	227	§	15[**] (4.88×10^{-13})
	228	§	15[**] (1.83×10^{-11})
	230	§	15[**] (7.29×10^{-7})
	232	§	15[**] (1.37×10^{-1})

Element (Symbol)	Radionuclide/ Isotope (Mass Number)	Minimum Detection Limits[*] pCi/L (mg/L)	Maximum Contaminant Levels in Water[†] pCi/L (mg/L)
Uranium (U)[¶]	234 §	1.5 (2.41×10^{-7})	15 (2.41×10^{-6})
	235 §	1.5 (6.9×10^{-4})	15 (6.9×10^{-3})
	238	1.0 (0.003)	10 (0.03)
Natural Uranium (U)[¶ §]	—	2.0 (3.0×10^{-3})	20 (0.03)
Gross alpha (α)	—	3	15[†] (N/A)
Gross beta (β)	—	4	4[†] mrem/y (N/A)

[*] 40 CFR 141 (EPA, 2002)

[§] The MDCs for these radionuclides are 10 percent of the concentration required for an individual whole body dose of 4 mrem/y (for β/γ emitters), 15 pCi/L for α emitters (except ^{238}U), or 0.03 mg/L (for total uranium), based on a daily intake of 2 L of water. As an example, this would be about 10 pCi/L (8.8×10^{-12} mg/L) for ^{60}Co.

[†] Only radium and uranium have MCLs (EPA, 2002). Values for the other radionuclides are derived from the gross alpha and gross beta MCL values. To avoid exceeding the MCL, the total gross alpha or gross beta radionuclide activities should not exceed 15 pCi/L.

[‡] The limit for ^{226}Ra + ^{228}Ra is 5 pCi/L.

[**] Assumes that the gross alpha concentration limit applies to each isotope.

[¶] If uranium is determined by mass-type methods (i.e., fluorometric or laser phosphorimetry), a 0.67 pCi/µg uranium conversion factor must be used. This conversion factor is based on the 1:1 activity ratio of ^{234}U to ^{238}U that is characteristic of naturally occurring uranium in rock. The actual relationship between uranium mass concentration (µg/L) and activity (pCi/L) varies somewhat in drinking water sources, because the relative amounts of the radioactive isotopes that make up naturally occurring uranium (^{238}U, ^{235}U, and ^{234}U) vary among drinking water sources. The typical conversion factors that are observed in drinking water range from 0.67 up to 1.5 pCi/µg.

The drinking water regulations lists the "maximum contaminant level" (MCL) for each radionuclide as the concentration (in pCi/L) that would result in a dose of 4 mrem/y if ingested. MCLs are often risk-based cleanup levels. OSWER Directive 9200.4-18 (EPA, 1997) provides guidance on establishing risk-based protective cleanup levels for Superfund sites contaminated with radiation. For each emitter that is detected by the laboratory, the analyst must divide the pCi/L found in the sample by the value in the conversion tables. This provides a fraction of how much the particular beta or photon emitter is providing towards the maximum of 4 mrem/y for all of the beta photon emitters (EPA, 2002). In order to ensure that the 4 mrem/y dose limit is not exceeded, the sum of the individual fractions (for each radionuclide) should not exceed 1.0. Table 1 identifies the minimum detection limit (also referred to as the "required detection limit," or RDL) that any radioanalytical method must have in order to be acceptable for processing samples for that radionuclide. The example below demonstrates the calculation of the sum of fractions for a sample containing strontium and tritium:

Radionuclide	MCL (pCi/L)	Sample (pCi/L)	Fraction
^{90}Sr	8	6	0.75
^{3}H	20,000	8,000	0.40
		Sum of fractions:	1.15

Although each radionuclide individually is less than its respective MCL, the sum of the fractions is greater than 1.0. Therefore, this would not be an acceptable water source. Facilities that discharge radionuclides in their wastewater streams, have limits identified in 10 CFR 20 based on the radiation dose calculated by analyzing environmental pathways. The effluent concentration values noted here are from 10 CFR 20 (Appendix B, Table 2, Column 2), and have been converted to pCi/L. These values are included here as a reference. Specific effluent limits for individual sites would be established based on the requirements of the project.

2 Overview of a Cleanup Process and Radiological Methodologies

Radioactive contamination in soil and water can be determined by several different laboratory methodologies. However, the type of site, the stage of the project that is being investigated, the levels to which the contamination is to be determined at that site, and the specificity of the analyses needed, will determine which of these methodologies will be appropriate. Methodologies used for determination of radioactivity can be placed into three broad categories:

- Screening,
- Routine, and
- Specialized.

Each of these methodologies may be appropriate at different stages of a cleanup process. The greatest selectivity for radionuclides will lie in the specialized methodologies. These generally will be the most expensive and take the longest amount of time to perform.

2.1 Laboratory and Field Screening Methodologies

Using screening methodologies, it is possible to identify sites requiring immediate actions, as well as areas requiring additional investigation. The screening methodologies may also allow the site investigation team the insight into choosing which more sophisticated methodologies or analytical techniques may be required.

Screening methodologies will generally be relatively quick (minutes to hours), are not radionuclide-specific, require instrumentation that is not sophisticated and can be used with a minimal degree of user training. An additional advantage is that considerable time is saved, because these techniques do not employ chemical separations. Thus, it would be considered a limited-scope assessment intended to determine the potential of the site for significant harm to public health or the environment.

Site-specific action levels that are established early in the cleanup process may be adjusted as additional data are assessed. Preliminary screening levels may initiate immediate response activities, or may indicate that radionuclide-specific methodologies should be used for more definitive measurements. For example, emergency response or removal could be triggered by the results of a screening method above a certain threshold. The action levels may need to be flexible enough to expand the scope of investigation for potential radionuclides so that the initial assessment can accurately depict the problem. More detailed information on these detection methodologies is provided in Section 4.

2.1.1 Gross Alpha and Gross Beta Methods

Gross screening methods are applicable when the MCL or derived concentration guideline level (DCGL) of the radionuclide of interest is much greater than the concentrations of the total background radionuclides in the sample. These methods can identify the presence of radionuclides that emit alpha or beta particles. The measurement made will identify the total number of particles detected per unit time (e.g., per minute). However, it does not identify the amount or type of each radionuclide that may be present. It allows the comparison of measurements in the suspect area to measurements in nearby areas that are known to be free of the contamination under investigation. Because the specific identity of the radionuclide may not be a principal concern at this point, this analysis will identify the overall extent of the contamination in terms of gross quantity (measured in counts per minute, cpm) and areas affected (in land area measurement units as well as depth profile). If the gross-screening method is calibrated using a reference radionuclide, then analytical results will be reported in disintegrations per minute.

Detection methods commonly used for making screening measurements include:

- Alpha/beta survey-type detectors (usually hand held);
- Gas flow proportional counters;
- Liquid scintillation detectors; and
- Other devices that have a thin "window" (i.e. the detector covering) that will allow the emitted particles to interact with the detector.

These detection devices can differentiate between alpha particles and beta particles because their energies on the detector are significantly different. However, without chemical separation, no significant information about specific radionuclides can be gained by the gross alpha or beta count rates.

Individual radionuclides will be either alpha or beta emitters (most of these will also emit gamma radiation as a result of the alpha or beta decay). Alpha or beta particles emitted by different radionuclides may not have the same energies, and this will result in different detection efficiencies.

Two examples of how these methods might be valuable will help to identify the conditions under which they may be used.

Example 1. An old manufacturing process for luminescent dials used ^{226}Ra. The storage area for the radium was in the basement of the building (3 m below grade), which has since been filled in with soil. It is necessary to determine the gross level of activity prior to site excavation to assess subsequent worker hazards. An *in situ* measurement of radiation at grade using a hand-held device would most likely not yield useful information because ^{226}Ra is principally an alpha emitter (see Table 2), and these emissions would not penetrate the soil. The progeny of ^{226}Ra are all alpha and beta emitters, and their decay emissions would also be shielded by the soil depth. However, thinly sliced segments of 3-m borings, could be measured individually in the field with a α/β survey meter, or in the lab with a GP detector.
Example 2. A well located 0.5 km from the site in Example 1 may be affected by the radium in the soil. Samples of the water may be analyzed at a laboratory without any sample preparation. A liquid scintillation counter can be used for gross alpha determination, by appropriate adjustment of the instrument for alpha response.

As shown in these examples, some types of screening methodology may not be applicable to certain types of samples. For example an α/β survey meter would not be readily applicable to a screening analysis of water samples for alpha emitters, nor would a liquid scintillation detector be applicable for direct analysis of soils. The alpha/beta survey methods can be used in the field as well as in the laboratory. The other methods are easily adaptable to field laboratories.

2.1.2 Gamma Analysis

Four distinct detection methods exist for screening-level gamma analysis:

- Geiger-Mueller (G-M) detector with a “beta shield”;
- Cesium iodide [CsI(Tl)] detector (usually found only at research laboratories);
- Sodium iodide [NaI(Tl)] detector; and
- Germanium (HPGe) detector.

The four detection methods listed above are in order of increasing specificity and decreasing ease of field measurement. The G-M detector with the beta shield closed will yield information regarding gamma emitters above a certain energy threshold (~100 keV depending on the thickness of the beta shield). The beta shield is a piece of metal (either steel or aluminum) that will absorb betas so they do not interact with the gas-filled chamber of the counter. No information on the range of gamma energies or the specific radionuclides would be available from this technique. The instrument is hand held and needs no auxiliary equipment. The CsI(Tl) detector has low-energy resolution for gamma rays in the energy range of ~20 keV to 3,000 keV. It is very efficient, but it can only resolve peaks that are on the order of 150–200 keV apart.

The NaI(Tl) detector is sensitive in the range of ~20 keV to 2,500 keV, depending on the detector housing thickness and size of the detector. It can provide general information regarding the distribution of energies of the gamma emitters in the samples, and has a very high efficiency. However, it most likely cannot provide specific radionuclide identification. This is due to its limited ability to distinguish gamma rays that are less than ~50 keV apart. Newer instruments can be hand held, but older ones may need a high voltage power supply and cables.

The HPGe detectors can provide significant details regarding specific gamma emitting radionuclides. It can distinguish gamma rays that are within about 1.5 keV of each other. A recent application for this type of detection system is called ISOCS (“In Situ Objects Counting System”). This unit is field-portable, is mounted on a rolling cart, and requires a high-voltage power supply and a supply of liquid nitrogen or an electronic cooling system.

Obviously, if the analytes in question are not gamma emitters (or weakly gamma emitting; see Table 2), then using this screening method may not provide useful information. These methods are used routinely in the laboratory. However, several adaptations to the detection system hardware exist that allow them to be used in the field.

TABLE 2 — Radionuclides with low-abundance gamma rays

Radionuclide	^{89}Sr	^{90}Sr/^{90}Y	^{241}Pu	^{242}Pu	^{129}I	^{252}Cf	^{226}Ra
Principal Decay	β^-	β^-	β^-	α	β^-	α	α
Gamma, keV	909	1761	149	44.9	40 (32 X-ray)	43 (100)	186 (262)
Abundance, %	9.5×10^{-4}	1.1×10^{-2}	1.9×10^{-4}	4.2×10^{-2}	7.5 (92.5)	16 (0.2)	3.3 (5×10^{-3}
Radionuclide	^{241}Am	^{237}Np	^{232}Th	^{243}Cm	^{228}Th		)
Principal Decay	α	α	α	α	α		
Gamma, keV	59.5	86.5	911 (from ^{228}Ac)	278	84		
Abundance, %	35.7	12.6	27.2	14	1.21		

Note: Several of these have additional, lower-abundance gamma rays as well

2.2 Routine Methodologies

In order to obtain radioactivity concentration for a specific radionuclide at environmental levels in either soil or water media, chemical separations usually need to be performed. Data collected by these routine methodologies are often used to characterize the concentration and distribution of radionuclides; assess risk to human health and the environment; and potentially select technologies for treatability testing to evaluate the performance and cost of the treatment technologies that are being considered for cleanup. Because each treatment effort may be radionuclide- and matrix-specific, a method that can differentiate the various radionuclides is important.

There are many different analytical procedures for separation of radionuclides from each other in water and soil matrices. In each case, the chemical (i.e., elemental) characteristic of the analyte is used for separating it from each of the other elements that may be present. Separation techniques, such as precipitation, electroplating, or evaporation, are used to minimize the volume of the sample fraction to be analyzed. At that point, the methods discussed in Chapter 5 (in greater detail) would be used to quantify the activity of the radionuclide present. The routine methods are identified in the next sections.

2.2.1 Gross Alpha and Gross Beta Methods

The analysis of radionuclides using these general methods of detection includes:

- Gas proportional counting;
- Liquid scintillation counting; and
- Cerenkov counting (high-energy beta counting).

Each of these methods relies on effective chemical separation to determine low-level activity and discriminate specific radionuclides (i.e., eliminate other radionuclides that might yield a positive count rate when the radionuclide of interest is not present). Their major advantages are that these methods generally have high detection efficiency and may minimize the sample counting time to achieve a specific MDC. Their disadvantage is that they lack the energy discrimination necessary to distinguish alpha or beta particles of different energies.

2.2.2 Spectrometric Methods

The methods that can be considered spectrometric are:

- Alpha spectrometry;
- Gamma spectrometry [either HPGe or NaI(Tl)]; and
- Photon-Electron Rejecting Alpha Liquid Scintillation (PERALS®).

The most discriminating of these analyses is alpha and gamma (HPGe) spectrometry because of the high resolution of the solid state detectors they use. Thus, the identifying photon energies from ^{134}Cs and ^{137}Cs can be separated using gamma spectrometry, and the identifying alpha energies from ^{241}Am and ^{243}Am can be separated using alpha spectrometry. PERALS® can be used instead of alpha spectrometry, or a NaI(Tl) detector can be used instead of an HPGe when effective chemical separations are performed. They can be used to distinguish alpha particle energies that are ~150 keV different, and gamma ray energies as close as 50 keV, respectively. All of these methods are described in detail in Section 4.

2.3 Specialized Methodologies

The specialized methodologies discussed in this document are kinetic phosphorimetry analysis (KPA) and mass spectrometry. In contrast to measuring radioactive decay emissions, these specialized methodologies detect and measure the number of atoms of an element or isotope in a sample by either emission of UV radiation from an excited state or by atom counting, respectively. Mass spectrometry is used when there is a need to distinguish isotopes of the same element from one another. This becomes important when the contamination may be from different types of sources. For example, naturally occurring uranium is 99.27 percent abundant (by weight) in the ^{238}U isotope, 0.72 percent in the ^{235}U isotope and 0.006 percent in the ^{234}U isotope. Fuel used for nuclear power plants will be enriched in the ^{235}U isotope up to ~5 percent, weapons grade will be above 90 percent. Thus, the isotopic distribution of the uranium will help identify where it came from.

2.3.1 Mass Spectrometric Methods

Conventional techniques for radiochemical analysis are based on the chemical properties of radionuclides that allow them to be separated from all other stable elements in the mixture of the sample. At times it is extremely important to identify the specific isotopic mixture of some radionuclides (e.g., U, Pu, Np, and Am) in order to determine the source of the contamination.

Three different methods that are based on the same principle, charge to mass ratio of the ionized atom, can be used to identify the specific isotopic ratios of radionuclides. These are:

- Accelerator Mass Spectrometry (AMS);
- Thermal Ionization Mass Spectrometry (TIMS); and
- Inductively Coupled Plasma-Mass Spectrometry (ICP-MS).

In each one of these methods, the sample is vaporized into its elemental constituents, the elements ionized and passed through a mass spectrometer. The distinct advantage of these methods is that the separation is based on the mass of the isotopes involved and not on their chemical nature. Thus, analysis of several different radionuclides, as well as different isotopes of a single element can be performed simultaneously. This type of analysis would most likely not be used in the initial phases of a site evaluation due to the specific nature of the analysis. However, during later phases, these methods could be used to collect site-specific data sufficient to characterize site conditions. They might also be used after remediation activities have been implemented to assess whether or not speciation of uranium or plutonium isotopes is necessary.

Currently, ICP-MS techniques are best suited for radionuclides with half-lives greater than about 10,000 years, when more sensitive analyses are required (such as for environmental levels of ^{239}Pu) or when isotopic analyses are required to separate isotopes whose decay emissions prevent separate quantification (such as ^{240}Pu from ^{239}Pu). Methods employing specialized radiochemical separations and the most sensitive mass spectrometers are currently being developed for radionuclides with shorter half-lives, such as ^{90}Sr.

2.3.2 Kinetic Phosphorimetry Analysis

KPA is a rapid method used primarily for the analysis of elemental uranium and thorium. This method relies on the electronic structure of the uranium and thorium ions in solution to establish valence orbitals that yield phosphorescent states. These states can be used to distinguish the uranium and thorium emissions from many other elements. Thus this method does not use the radioactive properties of these ions at all in determining their presence. The disadvantages are that—without chemical processing of the sample—the minimum detectable concentration is higher than by conventional radiation detection methods, and the measurement quality for these two elements is compromised because KPA does not distinguish isotopes.

2.4 Measurement Quality Objectives and Methodologies

Measurement quality objectives (MQOs) are the analytical data requirements of the data quality objectives and serve as measurement performance criteria or objectives of the analytical process for a specific project. MARLAP (2004, see Chapter 3) provides guidance on developing MQOs for selected method performance characteristics, such as method uncertainty at an analyte concentration, analyte detectability (minimum detectable concentration), minimum quantifiable concentration, applicable analyte concentration range, method specificity (ability to isolate one radionuclide from another), and method ruggedness. Each phase of the cleanup process for a site may have different MQOs. These MQOs will drive the specificity of the method or analysis to be used.

Referring to the example earlier in this chapter, suppose one MQO for the initial characterization was:

> Samples shall be analyzed to 15 pCi/g beta and 20 pCi/g alpha with a measurement uncertainty of 2.2 and 3.0 pCi/g, respectively, at those concentrations.

It certainly would be possible to apply routine methodologies for Ra, Pb, Bi, Rn and Po analyses and sum each of these to determine the total activity. One could also apply some of the specialized methodologies to the analysis of ^{226}Ra and mathematically estimate (conservatively) the activities of the remaining radionuclides from the ^{226}Ra decay chain. However, both of these approaches would be time consuming and highly specific, for an MQO that is more easily determined using a screening method. Later on during the site remediation and follow up activities, the MQOs might become more radionuclide specific such as, "the ^{226}Ra shall be analyzed to 1.5 pCi/g with a relative measurement uncertainty at that level of 20 percent." In this case, the necessary method would have to be able to eliminate the interference from all other chemically similar radionuclides, as well as hone in on ^{226}Ra specifically.

3 General Analytical Considerations

The information presented in this document on radioanalytical concepts takes into consideration the major source terms of the radioactivity generated by man-made processes at various sites throughout the country. The types of sites that this document is aimed at are:

- Department of Energy (DOE) and Department of Defense (DOD) site cleanup activities; and
- Naturally Occurring Radioactive Materials waste (NORM).

A summary of the important processes and radionuclides generated at each site will be discussed in subsequent subsections.

3.1 Site Source Term

This section discusses DOE cleanup sites and wastes containing naturally occurring radioactive materials. The decommissioning of commercial nuclear power facilities, and the required radionuclide analyses for that specific process, are regulated by the Nuclear Regulatory Commission (NRC, 2004) and are outside the scope of this report. However, for completeness, Appendix E provides an overview of issues associated with nuclear power plant decommissioning sites.

3.1.1 DOE Site Cleanup

Known as "legacy wastes," substantial amounts of radioactive wastes have been produced in the nation's nuclear weapons productions program since 1942. Wastes for this program resulted from the mining of uranium ore, extraction (milling) of uranium from the ore, ^{235}U isotopic enrichment of the uranium, and fabrication of uranium fuel from the enriched uranium to operate nuclear reactors for the production of $^{239/240}$Pu. The generation of the fissile materials of plutonium and uranium for the nuclear weapons program resulted in radioactive wastes at DOE sites throughout the country and at uranium mining and milling operational sites, mainly in the western states. Many of these facilities have had inadvertent releases that have led to environmental contamination. The radioactive wastes from the uranium mining and milling operations will be discussed under the subsection dealing with NORM waste.

Nuclear weapons production involves eight general groupings of activities including:

- Uranium mining, milling, and refining;
- Isotope separations (uranium enrichment);
- Fuel and target fabrication;
- Reactor operations;
- Chemical separations;
- Weapons component fabrication;
- Weapons operations; and
- Research, development, and testing.

Waste generated by chemical separations processes accounts for more than 85 percent of the radioactivity generated in the nuclear weapons production process. Waste is created by the acid dissolution of the spent fuel rods (and targets) from reactor operations and subsequent separation of the plutonium and uranium using a chemical process. Chemical separations operations were mainly conducted at the Hanford Site in Washington, Idaho National Engineering Laboratory (INEL) Site in Idaho, and the Savannah River Site in South Carolina.

According to DOE (1997a), there are 79 million cubic meters of contaminated solid environmental media associated with the nuclear weapons complex, of which 70 percent is contaminated with radionuclides. In addition, there are about 1,800 million cubic meters of contaminated soil, of which 57 percent is contaminated with radionuclides.

DOE has listed 38 sites that have more than 1,000 m^3 of contaminated solid media and 17 that have more than 100,000 m^3. Of the 38 sites listed, those with the greatest volume of waste (more than 1,000,000 m^3) are Fernald (Ohio), Hanford (Washington), Lawrence Livermore National Laboratory (California), Los Alamos National laboratory (New Mexico), Nevada Test Site (Nevada), and the Savannah River Site (South Carolina). The radionuclides in the waste and surrounding area at these sites vary according to the type of activity or operations conducted at the site. The radionuclides persisting at these sites depend on the amount of radioactivity produced during the operations and the nuclide's half-life. In some cases, a radionuclide with a half-life in years, such as tritium (^{3}H), with $t_{1/2} = 12.3$ y, or ^{60}Co, with $t_{1/2} = 5.27$ y, will be found in environmental waste if it was produced in significant quantities during operations.

As of 1991, the longer-lived radionuclides important for DOE site cleanup that are routinely analyzed are provided in Table 3. Some of the nuclides listed below may not be the result of operations but are included to be analyzed in the facility's standardized environmental monitoring program and, thus, may represent nuclides that are or were measured from atmospheric weapons testing conducted decades prior.

TABLE 3 — Longer-lived radionuclides at DOE sites

Facility	Soil	Surface Water	Ground Water	Sediment
Fernald	Uranium		^{137}Cs, ^{237}Np, ^{90}Sr, ^{232}Th, U	^{99}Tc, U
Hanford	^{137}Cs		^{137}Cs, ^{3}H, ^{129}I, $^{239/240}$Pu, ^{90}Sr, Ra	
INEL	^{137}Cs, ^{60}Co, $^{238/239}$Pu, ^{90}Sr		^{3}H, ^{129}I, $^{238/239}$Pu, ^{90}Sr	^{137}Cs, ^{60}Co, ^{90}Sr
Los Alamos National Laboratory	^{241}Am, ^{137}Cs, ^{3}H, $^{238/239/240}$Pu, ^{90}Sr, Th, U		^{137}Cs, ^{3}H, $^{238/239/240}$Pu, U	$^{239/240}$Pu
Nevada Test Site	^{241}Am*, ^{60}Co, ^{154}Eu*, ^{137}Cs, $^{238/239/240}$Pu*, ^{90}Sr, $^{235/238}$U	^{60}Co*, ^{3}H, $^{238/239/240}$Pu*	^{137}Cs, ^{60}Co, ^{3}H, $^{238/239/240}$Pu*, ^{90}Sr	^{137}Cs, $^{239/240}$Pu*
Oak Ridge National Laboratory	^{241}Am, ^{60}Co, ^{137}Cs, ^{244}Cm, $^{238/239}$Pu, Ra-228, ^{90}Sr, $^{232/233/234/235/238}$U	^{241}Am, ^{137}Cs, ^{60}Co, ^{244}Cm, ^{90}Sr, ^{3}H	^{137}Cs*, ^{3}H*, ^{60}Co*, ^{154}Eu, $^{238/239}$Pu, ^{90}Sr*, ^{99}Tc, ^{232}Th, $^{232/233/234/235/238}$U	^{241}Am, ^{60}Co, ^{137}Cs, ^{244}Cm, $^{238/239}$Pu, ^{90}Sr, $^{232/233/234/235/238}$U, ^{154}Eu
Rocky Flats	^{241}Am, ^{3}H*, $^{238/239/240}$Pu, $^{234/235/238}$U	$^{238/239/240}$Pu	^{137}Cs*, ^{3}H*, ^{90}Sr*, $^{234/235/238}$U*	^{137}Cs, $^{230/239}$Pu
Savannah River Site	^{137}Cs, ^{3}H, ^{129}I, ^{90}Sr	^{137}Cs*, ^{60}Co*, ^{3}H, ^{129}I*, ^{90}Sr*, $^{234/235/238}$U	^{137}Cs*, ^{60}Co*, ^{3}H, $^{238/239}$Pu, $^{226/228}$Ra, ^{90}Sr, $^{234/235/238}$U	^{3}H, $^{243/244}$Cm, ^{137}Cs, ^{129}I*, ^{90}Sr*, ^{228}Th, $^{235/238}$U

* Potential contamination not fully determined.
Source: OTA, 1991

3.1.2 Naturally Occurring Radioactive Materials Waste

Naturally occurring radioactive materials (NORM) are defined as those containing naturally occurring radionuclides—not produced by humans—in sufficient quantities or concentrations that require control for purposes of radiological protection of the public or the environment. In most cases, NORM may have been technologically enhanced in composition, concentration, availability, or proximity to people. NORM does not include source, by-product, or special nuclear material (related to the source term and products of the nuclear fuel cycle), commercial products containing small quantities of natural radioactive materials, or natural radon in buildings (Health Physics Society, www.HPS.org). The radioactive isotopes of uranium, thorium, carbon, potassium, polonium, lead, and radon are the principal radionuclides considered under NORM (Table 4).

TABLE 4 — Principal natural radionuclide decay series

Nuclide	Half-Life	Major Radiations
Uranium-238 Series	4.47×10^9 years	alpha, X-rays
Thorium-234	24.1 days	beta, gamma, X-rays
Protactinium-234m	1.17 minutes	beta, gamma
Uranium-234	245,000 years	alpha, X-rays
Thorium-230	77,000 years	alpha, X-rays
Radium-226	1,600 years	alpha, gamma
Radon-222	3.83 days	alpha
Polonium-218	3.05 minutes	alpha
Lead-214	26.8 minutes	beta, gamma, X-rays
Bismuth-214	19.7 minutes	beta, gamma
Polonium-214	164 microseconds	alpha
Lead-210	22.2 years	beta, gamma, X-rays
Bismuth-210	5.01 days	beta
Polonium-210	138 days	alpha
Lead-206	stable	
Thorium-232 Series	14.1×10^9 years	alpha, X-rays
Radium-228	5.75 years	beta
Actinium-228	6.13 hours	beta, gamma, X-rays
Thorium-228	1.91 years	alpha, gamma, X-rays
Radium-224	3.66 days	alpha, gamma
Radon-220	55.6 seconds	alpha
Polonium-216	0.15 seconds	alpha
Lead-212	10.64 hours	beta, gamma, X-rays
Bismuth-212	60.6 minutes	alpha, beta, gamma, X-rays
Polonium-212	0.305 microseconds	alpha
Thallium-208	3.07 minutes	beta, gamma
Lead-208	stable	
Non-Series Radionuclides		
Potassium-40	1.28×10^9 years	beta, gamma

These radionuclides, and more than a dozen other radioactive elements, are present in rocks, soils, building materials, consumer products, foods, and industrial wastes generated from mining, oil and gas extraction, mineral extraction, and geothermal wells. Commercial and consumer products, such as lawn fertilizers, watch dials, smoke detectors, gas lantern mantles, ceramic glazes, and air filters, may contain the long-lived radionuclides of uranium, thorium, radium, and polonium.

Regulators are most interested in the large amount of NORM waste generated from industries conducting metal mining and processing and oil and gas extraction processes. On an annual basis, these industries generate nearly a billion metric tons of NORM waste. More recently, programs have been established by the state regulators and EPA to address the technologically enhanced, naturally occurring radioactive materials (TENORM) wastes from these industries. (See www.epa.gov/radiation/tenorm/about.htm).

The TENORM waste matrices that are evaluated include surface and ground water, produced waters (effluents), soil, sediments, sludge, and mineral (barite) scale from pipes or conduits. The concentrations of the NORM radionuclides vary according to geographical location and chemical processing and extraction practices. For example, the ^{226}Ra concentration in produced water from the oil and gas extraction industries in Texas, New Mexico, Louisiana, and Mississippi typically ranges between about 1 and 1,000 pCi/L. Additional information on TENORM can be found at the following websites:

- www.tenorm.com/bkgrnd.htm
- pubs.usgs.gov/fs/fs-0142-99/
- pubs.usgs.gov/fs/fs-0142-99/fs-0142-99.pdf (concentration of NORM in oil and gas industry)

With two exceptions, TENORM and NORM are regulated primarily by individual state radiation control programs and not by federal agencies. Exceptions include the transportation of NORM-containing wastes (subject to U.S. Department of Transportation regulations) and NORM management activities (may be subject to regulations promulgated by the Occupational Safety and Health Administration, e.g., www.rrc.state.tx.us/divisions/og/key-programs/norm.html). The state regulatory requirements applicable to TENORM or NORM-containing wastes can be reviewed on the State Regulations and Guidelines page of the website (www.tenorm.com/regs2.htm#States). Several organizations have been actively developing guidance on the regulation of NORM. The Conference of Radiation Control Program Directors maintains suggested state regulations for control of radiation, available at www.crcpd.org/SSRCRs/TOC_4-2004-on-line.pdf.

The principal radionuclides of concern for TENORM are from the three naturally occurring decay series of ^{238}U, ^{235}U, and ^{232}Th, and the long-lived radionuclide, ^{40}K. Table 4 lists components of the uranium and thorium series, along with ^{40}K. Generally, the ^{235}U (known as the actinium series) series does not play a significant role in industrial TENORM due to its very low presence (1/20 of the radioactivity concentration of ^{238}U) in the natural environment. The radionuclides in the decay series attain a state of secular radioactive equilibrium (see Appendix B) if not subjected to chemical or physical separation. Technological enhancement of NORM as well as natural, physical, and chemical reactions in the environment often interfere with this equilibrium balance.

3.2 Sample Preservation and Transport

The entire process of transporting water and soil samples from the sample site to the laboratory should be carefully planned. Project planners should discuss with the contract laboratory specifics about sample container types, sample volumes or masses required for each analysis and matrix, and preservation techniques to be used for each matrix/radionuclide combination. Container or sample integrity can be compromised if the sample temperature becomes too high or too low. In either case, the sample may be damaged if temperature variations cause too much stress. The sample integrity must be carefully considered prior to performing an analysis. The sample preservation requirements should be part of the project's analytical protocol specifications (APSs). General information regarding this aspect of sample handling can be found in MARLAP (2004), DOE (1997b), 40 CFR 136 Table II, and ASTM Volume 11.02 (requirements specified for each radionuclide within its procedure).

In addition, when a container is broken, other samples can be affected because shipping labels (sample identification) are obscured or because the other sample's integrity is compromised by contamination from the sample that leaked. Personnel who collect the samples should ensure that the sample containers are firmly sealed, and that the samples will not experience extremes of heat or cold during the transport based on the type of vehicle, the route, and the estimated time of the trip. Simply shipping samples in ice packs, or insulation will not ensure that they will be protected from temperature extremes.

3.2.1 Water

The chemical concentration of radionuclides in water samples is extremely small. For non-radioactive materials, trace quantities are measured in the part-per-million (ppm) to part-per-billion (ppb) range. Radionuclides at environmental concentrations are 6 to 12 orders of magnitude lower in mass concentration than this. At these very low mass concentrations, oxidation-reduction, complexation, and volatilization reactions can occur, which can change the chemical identity of a species in solution. These reactions can lead to irreversible deposition of radionuclides on the container wall. Small mass losses of radionuclides to the container walls during transport and storage can significantly affect their measured concentration. It is extremely important, therefore, that appropriate preservation techniques be specified in the sampling documents for the project.

For most radionuclides identified in this document (with the exception of carbon, hydrogen, and iodine), preservation of the water sample at the sample site will include some form of acid preservation using HCl or HNO_3 to less than pH 2.0. There are three different possible points at which to acidify the samples:

- Acid is added to the sample vessel prior to the introduction of the sample;
- Acid is added to the sample after filtration at the sample site; and
- Acid is added to the sample after filtration in the lab (this requires a very short transit time from the field to the laboratory, usually only a few hours).

The process to be used for preserving samples generally is stated in the project statement of work (SOW) and the APS. The decision as to when to filter or preserve must be based on the project specific measurement quality objectives.

In addition to acidification, other sampling requirements such as the type of container, the storage temperature, and the storage period may be specified. These requirements will depend on the expected chemical nature of the radionuclide and the chemical nature of the sample medium. Storage containers are generally Teflon or high-density polyethylene. The composition of the sampling container is also important because:

- Some containers are more susceptible to radionuclide adsorption;
- Glass presents breakage concerns during shipping and handling;
- Glass containers also contain NORM which may leach in the acid environment and raise sample background counts; and
- Some containers (e.g., polystyrene culture flasks) are not stable with the concentrations of added acid necessary for preservation.

When required and specified, a typical storage temperature is usually 4 °C. This is usually only necessary when biological activity may alter the chemical species of the radionuclide or when volatile radionuclides (such as ^{14}C) or any radioiodines are present.

Additional sample preservation requirements may be necessary for certain radionuclides (elements), depending on the nature of the sample and the specific radionuclide being sampled. Some of these considerations are:

- Addition of carrier or tracer;
- Addition of oxidizing or reducing agents; and
- Elimination of air space in sample bottle.

This may be important for the isotopes of S, P, Tc, U, C, I, and Pu in certain matrices. There are four exceptions to the preservation described above. When sampling and analyzing for these radionuclides in particular, the laboratory and the field-sampling personnel must communicate the exact methods being used by each so that there is continuity in the sample-preservation process. This is usually done in the APS or the SOW.

- Hydrogen (specifically tritium, designated as T) in environmental water samples will almost certainly be present as H-O-T. The only preservation methodology recommended for samples that are to be analyzed for T is to reduce sample temperature to 4 °C as soon as possible. Addition of acids to the sample may interfere with subsequent laboratory analysis. Plastic containers should not be used for tritium samples with very high specific activity (curie levels and above).

- Analysis for ^{14}C in environmental water samples can deal with several different chemical carbon forms. The two most prevalent are carbonate and bicarbonate. In both cases addition of acid to preserve the sample will result in these species being transformed to CO_2 and the expulsion of the formed carbon dioxide gas from the sample. This will cause a loss of analyte. Presence of ^{14}C in organic molecules may be oxidized to carbon dioxide by addition of acid, also causing loss of the analyte. Here again the only recommended technique for preservation would be to reduce sample temperature to 4 °C as soon as possible. However, some projects have used a mildly alkaline solution of NaOH or NH_3 to prevent losses of ^{14}C by maintaining the carbon in its carbonate (CO_3^{-2}) form.

- Iodine analysis in environmental water samples presents a significant challenge because it may exist in as many as six different oxidation states. Iodine is also subject to conversion to volatile I_2 in acidic solutions containing oxygen. For these reasons, it is advisable to add iodide carrier and thiosulfate (or an equivalent reducing agent) to minimize loss of iodine during sample preservation and storage. Consideration should be given to collecting samples for iodine analysis in glass versus plastic containers. Reduction of sample temperature to 4 °C is also recommended. A summary of preservation techniques that have been successfully employed for water samples is shown in Table 5. This is a general summary and specific preservation techniques should be based on project-specific data quality objectives or APSs.

- Polonium-210 should be preserved only with HCl at a pH less than 2.0.

It is also important to note that the amount of added acid or reagent may contribute to the overall sample volume. This should be taken into account when determining the sample volume so that an appropriate correction may be made.

TABLE 5 — Summary of preservation techniques for aqueous samples

Element*	Acid pH <2	Temperature	Base pH > 9	Reducing Agent	Oxidizing Agent
Americium	(HCl) HNO_3	4 °C			
Bismuth	(HCl) HNO_3	4 °C			
Carbon		4 °C	NH_3		
Cesium	(HCl) HNO_3	4 °C			
Cobalt	(HCl) HNO_3	4 °C			
Hydrogen		4 °C			
Iodine		4 °C	NaOH	$S_2O_3^{-2}$	
Iridium[†]					
Lead	HNO_3	4 °C			HNO_3
Nickel	(HCl) HNO_3	4 °C			
Phosphorus	(HCl) HNO_3	4 °C			
Polonium	(HCl)				
Plutonium	(HCl) HNO_3	4 °C			$NaNO_2$
Radium	(HCl) HNO_3	4 °C			
Strontium	(HCl) HNO_3	4 °C			
Sulfur[‡]		4 °C	NaOH		
Technetium	(HCl) HNO_3	4 °C			
Thorium	(HCl) HNO_3	4 °C			
Uranium	(HCl) HNO_3	4 °C			

[*] Preservation techniques are generally specified to maintain the element in its most commonly occurring oxidation state as found in the environment. Project-specific APSs must be developed for each project, radionuclide, and matrix. This would include the concentration of the preservative, and (for example) the type of acid to be used.

[†] Iridium, because of its chemical inertness, will be in the zero valence state, and no specific preservation is better than any other.

[‡] Depending upon the type of sulfur compounds expected, basic solution may be the best preservative to prevent volatilization of sulfur as H_2S or SO_2.

3.2.2 Soil

Generally, there are no specific requirements for sample preservation for soil samples. However, two items should be considered before the start of any project. The first is to minimize the amount of air space that is in the sample container. This will minimize the potential for volatilization/oxidation of certain species. The second is to reduce the sample temperature to 4 °C as soon as possible to minimize any biological activity participating in elemental oxidation-reduction.

3.3 Parameters Affecting Quantification Using Radioactive Decay Counting Techniques

In order to quantify the activity of a particular radionuclide, several sample- and instrument-related parameters or factors are used:

- Sample size (mass or volume);
- Branching fraction (ratio) of the particle emission being counted (B). This is the fraction of all decays that result in emission of the characteristic radiation (alpha, beta or gamma);
- Counting interval (t), with the same counting interval for sample and background;
- Number of accumulated sample counts (C_{sample});

- Number of background counts for the equivalent sample count interval (C_{bg});
- Chemical yield of the analysis (Y);
- Detector efficiency (E) for the particular emission of the radionuclide [this is also affected by the detector and detection methodology];
- Decay constant of the radioisotope ($\lambda = 0.693/t_{½}$);
- Time intervals between sampling and beginning the sample count (T);
- Correction factor for radioactive decay of the radionuclide or its progeny during the counting interval (λt / $[1 - e^{-\lambda t}]$); and
- Correction factor for the ingrowth of progeny used to calculate the activity of a parent (I).

The concentration of a radionuclide in a sample (in units of activity per unit mass or volume) can be estimated through the following general formula and the specific analysis parameter or factor:

$$\text{Activity (pCi / L)} = \frac{[\mathrm{CF}][\mathrm{C}_{\mathrm{Sample}} - \mathrm{C}_{\mathrm{bg}}][\mathrm{e}^{\lambda \mathrm{T}}][\lambda \mathrm{t}]}{[\mathrm{t}][\mathrm{B}][\mathrm{Y}][\mathrm{E}][\mathrm{V}][1 - \mathrm{e}^{-\lambda \mathrm{t}}][\mathrm{I}]} \tag{1}$$

In Equation 1, *CF* represents a units conversion factor, and all other symbols are identified above. A different equation would be used when the instrument background is counted longer than the sample.

Although all of these parameters or factors affect the smallest amount of radioactive material that can be quantified (i.e., MDC), the two that the analyst can change to lower the MDC are the sample size and the counting interval. The sample size will have a one-for-one affect on the MDC, but not so with the counting time, because the counting time is related to the net decays determined. The term $[C_{sample}–C_{bg}]$ begins to approach zero when C_{sample} is only slightly greater than C_{bg} when the sample and background are counted for the same time. Due to the nature of radioactive decay, a statistical distribution (estimated by a Poisson Distribution) defines the possible counts that can be recorded in a certain time. In some instances, the background may have higher counts than the sample for the same counting interval. For more detailed information, review MARLAP (2004, Chapter 19).

3.4 Negative Results

The decay of radioactive atoms is a random phenomenon. The number of observed decays in a given time is characterized by Poisson statistics. The mathematical conclusion of this statistical function is that if we were to count the same sample for a limited number of successive intervals (e.g., less than 25), we would get a different number of counts each time. The range of values that we would observe would be $C_{sample} \pm t(C_{sample})^{½}$, where *t* is the parameter representing the degree of confidence in the measurement result. This relationship is true for both sample and background measurements. As the counting time increases, the number of observed detector events will increase, but the average count rate (counts/unit time) remains approximately the same. However, the relative uncertainty of the measurement — $[C_{sample}]^{½}$ / $[C_{sample}]$ — will decrease.

If the background were counted for two different time periods, two different results would be expected. Although the background has not changed, the measurement results would vary because they are affected by measurement uncertainty and the random nature of radioactive decay.

If a sample's radionuclide concentration is very close to background, it is possible to have fewer counts in the sample than in the background, even when counted for an equal time period. In this case, the final sample value would be negative. (If the background and the sample are both counted several times, on some occasions the sample might have larger counts than the background. In this instance the sample activity would be positive.) Atom-counting techniques experience the same difficulties in measuring amounts of radionuclides close to the background level. The net signal detected from the sample (number of atoms) can be less than the measured background from blanks (or the instrument). This will also lead to the occurrence of a negative value for the analyte.

Two conclusions can be drawn about negative sample values. First, when analytical results yield negative values, the radionuclide concentration will be very small—approaching that of background. Second, to minimize the possibility of reporting that no activity is present when some exists (a "Type II" decision error, sometimes referred to as a "false negative"), the count time or sample size may need to be increased (i.e., more atoms are present) to improve the statistics and reduce the relative uncertainty of each measurement. For more detailed information, review MARLAP (2004, Chapter 19).

3.5 Measurement Uncertainty

The term "uncertainty" refers to a lack of complete knowledge about something of interest. The radioanalytical process requires several different measurements to be made. Each laboratory measurement involves uncertainty, which must be considered when analytical results are used as part of a basis for making decisions. Every measured value obtained by a radioanalytical procedure should be accompanied by an explicit uncertainty estimate. It is often stated that field sampling uncertainties are so large that laboratory measurement uncertainties contribute insignificantly to the total uncertainty. These claims may be true in some cases, however that is not a reason for failing to perform a full evaluation of the laboratory measurement uncertainty. A realistic estimate of the measurement uncertainty is one of the most useful quality indicators for a result.

Measurement uncertainty will be caused by random effects and systematic effects in the measurement process. Random effects cause the measured result to vary randomly when the measurement is repeated. Systematic effects cause the result to differ from the measured value by an absolute or relative amount. A systematic error is often referred to as "bias." Systematic effects may also cause the results to vary in a nonrandom manner. Generally, both random and systematic effects are present in the laboratory measurement process.

The measurement uncertainty of a sample result should not be confused with the error of a sample measurement. Error of the sample measurement is a theoretical concept that refers to the difference between the "true" value and the measured value. As the "true" value can only be estimated by repeated measurements, and because each measurement has its own uncertainty, the error cannot really be known or measured.

Some measurement errors are spurious errors, such as those caused by analyst blunders or instrument malfunctions. Spurious errors cannot be taken into account in the statistical evaluation of measurement uncertainty. They need to be avoided by the use of good laboratory practices. Such practices would be part of the analytical laboratory's protocols or procedures, which would be written. Such documents should also have a method for detecting such errors and a means through which they are corrected by appropriate quality assurance (QA) and quality control (QC) activities.

For example, consider a laboratory analysis that yields a value of 100 pCi/Liter for ^{137}Cs. Assume that we "know" the true value to be 110 pCi/L. The error would be –10 pCi/L. However, we do not know exactly the true value or the measured value. We can ascertain how uncertain we are of both values by the uncertainty in the measurements. Measurement uncertainty is the parameter that analysts use to judge the precision of the analysis. A statistical parameter associated with the uncertainty is the confidence level. The confidence level tells the analyst how sure he is of the measured value. It is based on the standard deviation of the analysis and is constant. This uncertainty is often expressed as a ± value after the analytical result and stated to be at a certain confidence level.

For the same example, assume that the value was reported as 100 ± 25 pCi/L, the uncertainty is at the 95 percent confidence level, and there is no measurement bias. The "true" radionuclide concentration value of the sample would be within the 95 percent confidence interval (75 to 125 pCi/L) that has been established for the measurement. In addition, if the sample were to be repeatedly re-analyzed using the same method, 95 percent of the measured concentration values would be within the confidence interval. The reported measurement uncertainty for an individual analysis should be consistent (same magnitude or less) with the required method uncertainty for the radioanalytical method and sample matrix as defined in the measurement quality objectives (MQOs).

Several different measurements may be made on a sample in the laboratory, all of which contribute to the measurement uncertainty. (Uncertainties associated with sampling are very complex and are not within the scope of this report.) The following is a list of some of these sources:

- Mass or volume of the sample;
- Sample counts;
- Background counts;
- Tracer (counts) or carrier (mass);
- Decay correction; and
- Chemical yield.

In addition to these, some of the indirect contributors to the measurement uncertainty are half-life, detector efficiency, and the branching fraction of the radioactive particle.

The total measurement uncertainty of a radioactivity measurement may be expressed mathematically as the partial derivative of the radioactivity value with respect to all the input parameters that determine it. It is unnecessary to pursue this exact mathematical derivation in this document (MARLAP, 2004, Chapter 19). However, it is important that full consideration be given to each of the input parameters to equations like Equation 1 on page 20 and how they impact the total measurement uncertainty. The project planning document should identify how the measurement uncertainty will be calculated.

3.6 Sample Analysis Turnaround Time

Turnaround time is an important aspect of the overall analytical process that is often overlooked in the planning phases of a project. The elements of this part of the process are:

- Sample receipt by the laboratory;

- Sample preparation before analysis;
- Analytical separation process;
- Sample counting; and
- Data review and report generation.

Depending upon the specific analysis, these elements can take a significant period of time: a week or more is a common turnaround time for these analyses. Each of these elements is explained in the subsections that follow. The time involved in determining the mass of a sample, or precipitate is usually between 5 and 20 minutes and is not included in the discussion below.

The term "constant weight" is used in many protocols. This is a repetitive process requiring, at a minimum, two cycles of drying, cooling, and weighing. This process will take a minimum of 2½ hours to as long as 8 hours, depending on the nature of the sample and its water content.

An estimate of the amount of time for single-sample analysis for each element for specific methodologies is provided in the tables in Appendix D. These times can be affected by the skill of the analyst, the complexity of the matrix, and the detection sensitivity desired. These times also represent no delays between sample cataloging, digestion, separation, and counting in the laboratory. (Note that the analysis times in these tables do not include data verification/validation or report generation and approval. Routine turnaround times for final reporting of sample results is usually 30 days; "expedited" is two weeks, and "rush" reporting is one week.) Specific methodologies that change these times and detection capabilities are currently being developed.

3.6.1 Sample Receipt by the Laboratory

In every instance of sample transfer to a contract laboratory, sample receipt is critical, because it establishes the sample integrity, identity, and suitability to be analyzed for the radionuclides in question. The receiver must verify the number of sample bottles, their identity and container integrity as compared to the chain-of-custody form that accompanies the samples. For certain samples, a radiation survey of the shipping and sample containers may have to be performed. In addition, any preservation requirements must be verified as acceptable. All anomalies must be noted by the laboratory and should be verified with the remedial project manager or on-scene coordinator (or equivalent) before any laboratory processing occurs. Once accepted, the samples are entered into the laboratory's data management system. The total time that this step takes can be several hours, depending upon the number of samples being transferred to the laboratory.

3.6.2 Sample Preparation Before Analysis

Most samples require preparation prior to performing the separation of the radionuclides of interest from all the other elements in the sample matrix. Two separate examples identify the types of sample preparation that may be needed. These examples focus on the laboratory aspect of sample processing. Other sample constituents can affect sample holding time, preparation, and separation. The presence of paints, VOCs, PCBs, chromium, or lead may significantly affect sample holding times (required for nonradioactive analytes in the sample) as well as sample preparation prior to processing. The manner in which the samples are handled by field and laboratory personnel will need to be considered if these types of hazardous materials may be present. Thus, it is important that planning documents effectively communicate these facts to personnel handling and processing these samples in the field as well as in the laboratory.

Example 1: Tritium Analysis in Water and Soil

Analyzing tritium in water requires elimination of as much chemical interference as possible in the sample by distilling the water before liquid scintillation analysis. The distillation process should take between 30 minutes and 1 hour for laboratories that are set up to perform this analysis.

In the instance of performing tritium analysis on a soil sample, the sample must be passed through a sieve of uniform size as determined by the APSs of the project (this may have been done in the field or may be done in the laboratory, where it takes from 20 minutes to 1 hour). The soil must be weighed as received, then a measured amount of "clean" water, and acid or oxidant, added. A parallel sample must be dried at 105 °C to achieve constant weight, thus allowing the determination of moisture content of the soil sample as received. The sample with "clean" water and additives is then allowed to equilibrate for up to 12 hours (dependent upon the APSs), before distilling the water from the sample.

Example 2: Americium Analysis in Soil

Soil samples containing americium require the same sieving steps as tritium to ensure that the particle size meets the APSs. The sample will then be dried to constant weight and then may either undergo combustion in an oven (3-8 hours) or wet acid digestion (2-6 hours). In both cases, the purpose is to remove the extraneous organic material in the sample and solubilize the americium (the oven combustion is followed by acid dissolution).

Inherent to any sample preparation process is ensuring that all ions of the analytes are in the same oxidation state or chemical form, and that any tracers or carriers have been added. This part of the sample preparation can take up to one hour to complete, depending on the number of possible different oxidation states or species of the analyte that may be present.

3.6.3 Homogeneity and Adequate Sample Preparation

This aspect of the sample needs to be defined in the project APSs and SOW. It identifies how to assess if the sample is homogeneous to start, or if some physical adaptation must be performed.

If river water was sampled for the analysis of ^{60}Co, what are the sample homogeneity criteria we would be looking for? Cobalt can exist in both soluble and insoluble forms in the environment. Thus, an important consideration would be to determine if the sample had suspended matter, and what was the composition of the suspended matter. Some of the decisions that need to be made prior to taking the sample are:

- Should the sample be filtered?
- If the sample is filtered, should the suspended matter be analyzed?
- If the water and suspended matter are analyzed separately, should the final result be combined?
- If the sample is not filtered, what measures are taken to assure that the suspended matter is the appropriate fraction of the water taken for analysis?

A similar set of decisions needs to be made for soil samples:

- Is plant material removed from the sample? Analyzed separately?
- Does the soil need to be ground to a uniform size (and what is that size)?
- Should stones above a certain size be removed?

- Should the soil be weighed as is, or dried at a certain temperature?

The APS also should identify the sequence for drying, mixing, and removing a portion of the soil for analysis. For example, "The whole sample as received is to be dried at 110 °C, then sieved through an 8-mesh (2.38 mm) screen. The resultant material should then be blended for 15 minutes in a ball mill. A separate portion of approximately 10 percent of that final mass is removed for analysis."

Sample homogeneity and representative subsampling are extremely important when relating the final results of analytical techniques that use different masses of sample for analysis. For example, gamma spectrometry typically requires a large sample (100 to 4,000 g), while only 1 to 10 g is needed for alpha spectrometry. Inadequate sample homogenization or ineffective subsampling can result in misleading comparisons. Sample preparation and laboratory subsampling are discussed in detail in MARLAP (2004, Chapter 12, *Laboratory Sample Preparation*, and Appendix F, *Laboratory Subsampling*).

3.6.4 Sample Digestion

Once a homogeneous sample has been selected, digestion assures that all of the sample can be dissolved in one solution. The objective of sample digestion is to dissolve a solid sample quantitatively in water to produce a solution (homogeneous mixture), so that subsequent chemical separation and analysis may be performed. Because very few natural or organic materials are readily soluble in water, these materials routinely require the use of acids or fusion salts to bring the radionuclides into solution. These reagents typically achieve dissolution through an oxidation-reduction process that leaves the constituent elements in a more soluble form. In addition, each radionuclide to be analyzed, should be in a stable oxidation state prior to performing any chemical separations.

The three main methods of sample digestion for solids are wet digestion (using concentrated acids), salt fusion (using a solid flux melt and forming a single molten, nonaqueous phase with the sample) and combustion (using a stream of air in a high temperature furnace).

3.6.5 Oxidation State and Speciation of Radionuclides in Environmental Samples

Generally, analysis of environmental samples requires the total amount of a radionuclide present, regardless of what oxidation or speciation state it is in, to be determined. Certain elements can exist in more than one oxidation state. This means that before sample analysis begins, any carriers/tracers, and *all species* of an element are brought to the same oxidation state prior to any chemical separations being performed. This ensures that when we use carriers or tracers to monitor the chemical yield of the analysis, the amount of analyte and carrier/tracer recovered is the same percentage (see Equation 1 on page 20).

In some instances, it may be necessary to know the following information about the radionuclides as well:

- Different oxidation states of the radionuclides;
- Soluble versus insoluble fraction of the radionuclides;
- Chemical or molecular form (i.e., ionic or covalent bonding) of the radionuclides; and

- Chelating agents present that can complex the radionuclides.

The most accurate way to assess these parameters is to use direct analytical methods like anodic stripping voltammetry (ASV), ion chromatography (IC), ion selective electrode (ISE), Fourier transform infrared (FTIR), or UV-visible spectrometry (UV-VIS). However, these methods, with their conventional detectors, will require relatively large masses of the radionuclides (milligrams to micrograms, 10^{-3} to 10^{-6} g). Environmental samples typically have only picogram (10^{-12} g) to attogram (10^{-15} g) quantities of radionuclides.

Using conventional methods would require performing analysis on a split sample: one analysis for the total mass of the radionuclide, the other for a specific oxidation state that will remain unchanged by the procedure, such as mild acid dissolution or chelate leaching. This would be further complicated if several different oxidation states of the radionuclide are possible. (Such a case exists with plutonium, where as many as four different states (+3, +4, V, and VI) can exist simultaneously.) Thus, indirect methods, which require chemical separation and radiochemical analysis, may provide the most suitable method for determining chemical speciation.

Recent work in this area has coupled ion chromatography with ICP-MS instruments. The enhanced sensitivity using the ICP-MS technique allowed the eluent of the ion exchange column to be monitored continuously for samples whose transuranic concentration were in the range of pCi/L. Rollin and Eklund (2000) were successful in separating and quantifying U^{+4} and U(VI) in laboratory standards. Truscott et al. (2001) identified an unexpected change in oxidation state of uranium from VI to (+4) by using a reducing agent (Rongalite®) for plutonium. In these analyses of ocean water, the ion exchange columns were able to separate different oxidation states of neptunium, plutonium, and uranium.

Chemical speciation also can be performed by sequential aqueous extraction techniques that do not affect the oxidation state of the radionuclides during the extraction process (Schultz et al., 1998). Although the oxidation state of the transuranics are not identified specifically, the geological fraction of sediment that the radionuclides are associated with can be determined. This identifies the mobility of the radionuclides in the sediment environment.

There are other elements that also can be in multiple oxidation states in the environment in addition to the specific examples cited here. Table 6 summarizes the possible oxidation states of the radionuclides identified in this document. It is important to note that these radionuclides are "ultra-trace" components of the sample mixture (on a mass or molar basis), and the oxidation states of these ions can be affected significantly by the major sample ionic content. How rapidly changes can occur depends on several factors, including time, temperature of the medium sampled, temperature at which the sample is preserved, presence or absence of oxygen in the sample environment and its stored container, presence of bacteria, and sample degassing after being extricated from its matrix.

TABLE 6 — Summary of elements and their common oxidation states

	Oxidation State									
Element	**-2**	**-1**	**0**	**+1**	**+2**	**+3**	**+4**	**+5**	**+6**	**+7**
Americium						●		○		
Bismuth						●				
Carbon					○		●			

	Oxidation State									
Element	**-2**	**-1**	**0**	**+1**	**+2**	**+3**	**+4**	**+5**	**+6**	**+7**
Cesium				●						
Cobalt					○					
Hydrogen		○	○	●						
Iodine*		●	○	○	○	○		○	○	○
Iridium			●	○		○	○			
Lead					●		○			
Nickel					●	○				
Phosphorus						○		●		
Plutonium						○	●	○	○	○
Radium					●					
Strontium					●					
Sulfur	○				○		○		●	
Technetium							○			●
Thorium							●			
Uranium						○	○	○	●	

○ Allowable state ● Most common state

* The oxidation state of iodine depends significantly on the presence of other oxidizing or reducing materials.

3.6.6 Addition of Radiotracers or Carriers

A carrier is a stable (non-radioactive) isotope of an element that is chemically identical to the radionuclide of interest. A radiotracer is a radioisotope, not found in the type of sample being processed, which is chemically the same as the radionuclide of interest. Carriers or radiotracers may be added to monitor for the loss of a radionuclide during chemical processing. In some instances (e.g., technetium) neither a radiotracer nor a carrier is possible, and a surrogate is used (for technetium, it is usually rhenium).

The addition of carriers and radiotracers should be made as early on in the chemical analysis as possible, but before any chemical separations to the sample have occurred.

3.7 Chemical Separation Process

The chemical separation of the analyte from other chemical elements or compounds in the sample mixture is achieved through methods such as:

- Precipitation/filtration/centrifugation;
- Ion exchange;
- Complex formation;
- Solvent extraction;
- Oxidation-reduction; and
- Electroplating.

In many analyses, these methods are used in combination several times to achieve separation. Each of these methods individually can take several hours to complete. The longer times will be required when there are significant concentrations of interfering radionuclides.

In several different methods of analysis (^{90}Sr, ^{226}Ra, and ^{228}Ra are noteworthy), once a certain degree of separation has been achieved, the progeny of the radionuclide of interest are allowed to "grow in" so that the parent nuclide can be indirectly determined. This ingrowth period can take several hours to weeks, depending upon the half-life of the progeny.

A specific example of this type of method is used in the determination of ^{228}Ra. The particle emission from ^{228}Ra (5.8 y half-life) is a very low-energy beta that is poorly detected using gas-proportional counting. The first progeny of ^{228}Ra (^{228}Ac) has a short half-life (6 hours) and emits a beta particle of higher energy compared to ^{228}Ra, allowing better detection (quantification capability). Because actinium and radium are chemically different, they may not be in radioactive equilibrium in the environmental sample attained (see Appendix B). A separation of the radium is performed using a barium sulfate precipitation method coupled with a complex formation reaction to chemically isolate the radium from the actinium. This portion of the method will take 6-9 hours. At that point, the actinium is allowed to "grow in" in a matrix containing only radium. This process of ingrowth can take up to 36 hours, depending on the minimum detectable concentration desired. The actinium is separated from the parent radium through solvent extraction, ion exchange, or precipitation and counted.

3.8 Sample Counting

The length of time that a sample is counted will depend on two principal factors: the radionuclide's half-life and the minimum detectable concentration to be achieved. The previous section provides an example (Ra-Ac analysis) where the count time not only needs to take place immediately after the separation of the actinium from the radium parent, but counting for more than about 10 hours will not yield significantly better or more precise measurements. After a certain length of time, the activity of the short-lived ^{228}Ac will begin to approach the background activity (for low-activity samples).

Radionuclides with long half-lives (weeks to years) can be counted for as much as two days to help achieve the required minimum detectable concentration. Counting a sample longer than two days is not advisable, because changes in the background count rate may occur. Application of a background determined by a shorter counting time also may bias an analysis because it may not be representative of the background in a longer counting interval.

3.9 Data Review and Report Generation

The raw data must be converted to a final analytical value in the appropriate units (i.e., pCi/L or pCi/g), and a total uncertainty calculated based on the test parameters. A laboratory quality system will have certain requirements for data review, verification, and validation. This process ensures that there are no transcription errors, the calculations have been performed correctly, QC samples (splits, spikes, duplicates, etc.) are satisfactory, and the entire process of sample analysis meets the MQOs of the project. It usually also requires a manual calculation of the results for a small percentage of the data to ensure any computational errors have been fixed.

The length of this process will depend on the number of samples and the types of analyses that have been performed. However, for an individual radionuclide and one sample, the process can take as long as 20 minutes. The sum of the times for each of the individual sections stated here will yield the total turnaround time for just the laboratory portion of the process.

3.10 Units Used in Radioactivity Measurements

The traditional unit for measurement of radioactivity is the curie (Ci). This unit is equivalent to 3.7×10^{10} disintegrations per second (dps). This is the disintegration rate of 1 g of ^{226}Ra. The measurement of radioactivity in environmental samples is very small compared to this traditional unit, and frequently the unit used is picocuries (pCi), equivalent to 10^{-12} Ci. For water samples, the most commonly used concentration expression is pCi/L, for soil samples pCi/kg. It should be noted that some projects are now using units of pCi/g for reporting purposes. Other fractional units for the curie (such as "milli" and "micro") are also in common use. In recent years, the international community has switched to the becquerel (Bq) as the unit of radioactivity measurement. This unit is equivalent to 1.0 dps (see Unit Conversion Table on page xii).

The energy of radioactive particles is measured either in millions of electron volts (MeV) or thousands of electron volts (keV). The energies of both alpha and beta emitters are usually referred to in units of MeV, while gamma emitters are generally cited in keV. The range of energies generally examined in radiochemical analyses are listed in Table 7.

TABLE 7 — Energy range of radiochemical analyses

Alpha (α)	3 to 10 MeV
Beta (β)	0.005 to 4 MeV
Gamma (γ)	60 to 2,000 keV
Low-energy photon or X-ray	3 to 60 keV

The half-life of a radionuclide is the amount of time it takes for one-half of the initial number of radionuclide atoms to decay, leaving one-half of the initial radionuclide atoms remaining.. The unit for the measurement of half-life is variable, and there are not strict guidelines. Half-lives less than one hour generally are measured in minutes, those less than one day in hours, and those less than a year in days. Appendix B, Section B.1.3 (page 71) provides more details about half-life and decay.

3.11 Measurement Quality Objectives and Performance Testing

The measurement of radionuclides in water and soil samples can present significant challenges to the analyst because of the variety of matrix elements and compounds and the range of possible radionuclide concentrations. An MQO, for the processes covered by this document, is a statement that defines the radionuclide to be determined, the uncertainty of the measurement of that nuclide at a certain target concentration, the minimum detectable concentration (MDC) to be achieved for a particular radionuclide, and under what circumstances the radionuclide should be determined (see MARLAP, 2004, Chapter 3). As an example, consider the following statements as part of the APSs/MQOs for analysis of radium in ground water at a hypothetical remediation site:

- Radium-226 and ^{228}Ra are to be determined separately.
- Analysis can be performed in the presence of concentrations of up to 1,000 ppm calcium.
- At a concentration of 3.0 pCi/L, the method uncertainty at the 95 percent confidence level shall be 0.6 pCi/L.
- The presence of organic solvents at less than 100 ppm will not interfere with the analytical process.

These APS/MQO statements are both qualitative and quantitative. They show that the developer of the MQO has a basic knowledge of the materials to be analyzed, the site characteristics and the levels at which decisions will be made based on measurement uncertainties. Such statements (and perhaps more) would be required for each analyte.

Demonstration of the MQOs is usually a requirement of the project. Performance testing is a mechanism whereby the analysts are routinely presented with the project analytes in matrices that challenge the MQOs. These samples may be artificial or spiked, and can be prepared by an independent, outside laboratory or an independent branch of the analytical laboratory. Performance testing samples are different from the QC samples that will be measured as part of the overall QA process for the project, in that they provide evidence that the MQOs have been achieved. For the MQOs cited above, a performance testing sample might contain both isotopes of radium at a concentration of 1.0 pCi/L, with 500 ppm of calcium as a contaminant in the aqueous sample.

3.12 Selecting a Method

3.12.1 Performance-Based Method Selection

Typically, a laboratory will have developed and validated various methods to address the radionuclides, radionuclide concentration levels (environmental or effluents), and matrices expected from their customers and markets. However, a laboratory normally will select a particular radioanalytical method that will meet APSs contained in a statement of work or contract written by a client. The APSs include MQOs required for the laboratory's sample analyses, i.e., method uncertainty at a radionuclide concentration, MDC, minimum quantifiable concentration, method selectivity, etc. (MARLAP, 2004, Chapter 3). This type of method selection is referred to as "a performance-based approach to method selection." Performance-based method selection allows the laboratory to choose a method for processing samples as long as it can meet the required APSs and MQOs. Method performance for a project is demonstrated in the form of method validation documentation for the MQO requirements. During a project, ongoing method performance is monitored through performance evaluation programs, project-specific performance-testing samples or internal batch quality control samples. Additional information on laboratory method selection, project method validation and ongoing method evaluation can be found in MARLAP (2004, Chapters 6 and 7).

For purposes of this document, a "laboratory method" includes all physical, chemical, radiometric, and spectrometric processes conducted at a laboratory to provide an analytical result. Each method addresses a particular radionuclide in a specified matrix or, in some cases, a group of radionuclides having the same decay emission category (α, β, γ) that can be identified through spectrometric means. Depending on the category, a method may involve any or all of the following processes: sample preparation or dissolution, chemical separations, mounting the resultant product for counting, nuclear instrumentation counting, and analytical calculations. Multiple radionuclides in a sample may require different analytical detection techniques for which a laboratory may use a sequential separation method that addresses multiple radionuclides or stand-alone individual methods for each radionuclide. The APSs should ensure that certain parameters that affect method selection, such as sample preservation for each radionuclide and the sample size, are addressed.

3.12.2 Sources for Specific Method Information Available to the General Public

Major civilian laboratories and nuclear facilities include: Los Alamos National Laboratory, Lawrence Livermore National Laboratory, Brookhaven National Laboratory, Argonne National Laboratory, Pacific Northwest National Laboratory, Oak Ridge National Laboratories, Savannah River Site, and Hanford (all with DOE); DHS's Environmental Measurements Laboratory; and EPA's National Air and Radiation Environmental Laboratory. Certain departments or organizations within these laboratories have radiochemistry methods in the form of stand-alone standard operating procedures or within a manual. Each laboratory or specific department may have its own policy on the distribution of radiochemical methods employed for environmental matrices. In some cases, it may be easier to obtain an individual method rather than a manual compilation. The most direct way of obtaining methods is to contact the manager of the chemistry or environmental surveillance department.

4 Radioanalytical Methodologies

As discussed in Section 2, three general methodologies are considered important to the cleanup process: screening, routine radionuclide-specific, and specialized. The methodology selected for sample analysis in a particular phase of the cleanup process is related to the analytical protocol specifications/MQOs for the cleanup phase being conducted. This section addresses the typical methodologies to detect and quantify radionuclides in various matrices. Two modes of detection are discussed: radioactive decay emission measurements and atom counting measurements. Radioactive decay emissions measurements detect and quantify the α, β^-, and β^+ particles, electrons, X-rays, or γ rays emitted during the radioactive decay process. Because radioactivity is measured in terms of activity (becquerels, or disintegrations per second), measuring the detection rate for each type of emission (detections measured per unit time), together with information on emission probability of the type of emission, is the most direct way to quantify radioactivity. Radioactive decay emissions measurements come under the screening and radionuclide-specific methodologies. Atom-counting methods (Section 4.2) are the specialized methodologies that measure the number of radionuclide atoms directly or measure the light emissions from all stimulated atoms in an element. Given the number of atoms or mass of the radionuclide and its half-life, the radionuclide's radioactivity can be calculated (Appendix B, Section B.1.3, on page 71). Atom counting methodologies include mass spectrometry and kinetic phosphorimetry analysis.

The method selected depends upon the type of sample and the MQOs for the particular project, types of interferences that may be present, cost, and available equipment. Methods associated with routine radionuclide-specific and specialized methodologies may require some chemical separation prior to the final analysis to minimize interferences from other radionuclides and to concentrate the analyte into a smaller analytical sample. With the exception of drinking water, there are no "government-approved" methods for chemical separations used for the determination of radionuclides. However, the analytical techniques presented here are well established. Tables in Appendix D are set up for each element. Each table summarizes the detection techniques that are appropriate for each radionuclide, whether or not chemical separation is necessary, the routinely achievable MDC values, and the amount of time required to perform the chemical and data analysis. Important considerations affecting MDCs are explained in the box preceding the tables in Appendix D (page 80). These tables should be used as a general guide to selecting the methodology appropriate to the DQOs of the project.

4.1 Radioactive Decay Emissions Measurements

4.1.1 Gas Proportional Counting

Gas proportional counting (GPC) is capable of quantifying radionuclides emitting alpha and beta particles (with energies greater than about 150 keV) in small, dry test sources. Although this radiation detection method can differentiate between alpha and beta particles striking the detector, it does not have the resolution necessary to discern individual alpha or beta particle energies. Because of this, GPC is useful only for gross alpha and beta screening applications. The most common GPC configuration for evaporated water, soil, or air-filter samples of small residual mass is counting in a metal planchet between 1 and 5 cm in diameter and 0.3 and 0.6 cm in height.

Test-source masses are kept between 25 and 200 mg to minimize the self-absorption effects of alpha and beta particles in the source matrix. When there is a possibility of variable test-source mass, a detector-efficiency curve for a specific radionuclide is generated as a function of test-source mass. For gross alpha and beta counting applications, the accuracy of a result depends on matching the target nuclide with the nuclide used for calibration and the number of other alpha- and beta-emitting nuclides present in the sample. Measurement accuracies for gross alpha- and beta-particle counting are obtainable as low as 10 to 15 percent for single nuclides, but inaccuracies of 100 to 200 percent are not uncommon for mixtures of nuclides or heavy test sources. Data analysts should not expect that the gross alpha or beta activity in a sample will be equivalent to the summation of the individual activities of the alpha- or beta-emitting nuclides in the sample.

GPC also may be used for specific radionuclide analysis following radiochemical processing of a sample during the early investigation or remediation phases. GPC normally is applied to the measurement of ^{90}Sr, ^{89}Sr, ^{131}I, ^{210}Pb, ^{210}Po, ^{210}Bi, ^{228}Ra, and total (alpha) radium following chemical purification.

The typical GP detector backgrounds for alpha and beta particles are < 0.1 cpm and < 1 cpm, respectively. For most applications and nominal measurement times and sample sizes, the quantification capability is typically ≤ 1 pCi for alpha or beta measurements. With proper detector calibration, chemical-yield determination, and chemical isolation of the target nuclide, GPC can be very accurate for specific nuclides (a relative standard deviation of about 3 to 5 percent) when sufficient activity is present at levels greater than 100 times the detection limit.

4.1.2 Liquid Scintillation

Liquid scintillation counting (LSC) involves the detection of light generated by the interaction of charged particles with an aqueous solution containing organic molecules (i.e., a scintillator as a solute) that convert the absorbed energy into light photons. However, the detection of Cerenkov radiation, because of its production mechanism, does not require the use of an organic scintillator. A LSC is a low-resolution energy spectrometer that can distinguish between wide-banded alpha or beta energy regions. As such, most LSC analyses involve the measurement of a single radionuclide when possible, avoiding spectral interferences from other radionuclides. Analytical methods have been developed to process samples and provide a final test source matrix required for LS counting. This detection methodology is used for beta measurements involving very-low (18 keV) to high-energy (2,200 keV) beta-emitting radionuclides and for Cerenkov counting of high energy (> 1,000 keV) beta particle measurements. The typical applications of LSC are presented below.

Sample analysis by liquid scintillation counting methods may occur in all phases of the cleanup process, but its use as a screening methodology for α, β^- and β^+ particles is somewhat limited primarily to a clear water matrix having a minimum of chemical interferences. Application of the LSC as a radionuclide-specific methodology will be principally in the early investigation and remediation phases when the radionuclide has been identified. Because LSC is not a non-destruction sample processing method and is not a high-resolution spectrometer, sample analysis will require sample (non-aqueous) digestion and chemical processing for the radionuclide of interest.

4.1.2.1 Routine LSC Analysis

In routine LSC applications, a small-volume (1 – 10 mL) aqueous test source is combined with a commercially available organic scintillation cocktail (10 – 15 mL) and counted in a ~ 25 mL low-background plastic vial for a reasonable counting interval (e.g., 100 – 400 minutes). The aqueous test sources may include distilled water for tritium analysis to highly acid nitrate solutions for ^{90}Sr analysis. In some cases, a dry test source is added to the liquid or gel scintillation cocktail. Examples of these include the insertion of an air particulate filter paper into a liquid scintillation cocktail and the dispersion of dry $BaCO_3$ precipitate containing ^{14}C into a scintillation gel.

In order to prepare a test source for counting, a sample must be processed so that contaminants are removed or the radionuclide (element) is isolated from the sample and chemically purified. Solid samples must undergo a digestion or an acid leaching process to make the radionuclide available for chemical purification. Care must be taken to ensure that the chemical solution containing the purified radionuclide does not cause enhancement or degradation of the light output from the LS cocktail used. Typically, techniques for the measurement of changes in detector response due to chemiluminescence or phosphorescence (light enhancements) or quenching (light degradation from chemical agents or color) are incorporated in the instrument measurement protocols for the radionuclide method.

LSC is not as sensitive as other detection techniques for alpha and beta particle quantification. However, many of the detrimental physical parameters affecting other detection techniques are avoided with this detection technique, including test-source preparation problems and self-absorption and backscatter effects that cause variability in detector efficiency. The beta-emitting radionuclides important to environmental surveillance, effluent analysis, and site decommissioning and decontamination commonly analyzed by LSC include ^{3}H, ^{14}C, ^{55}Fe, ^{63}Ni, ^{99}Tc, ^{89}Sr, ^{90}Sr, ^{129}I, and ^{241}Pu. For intermediate levels of contamination, when the detection limit for the alpha emitting nuclides is higher than for low-level environmental levels, LSC can be used for the analysis of a single alpha-emitting radionuclide in a sample, such as ^{234}U, ^{235}U,^{238}U, ^{223}Ra, ^{224}Ra, ^{226}Ra, ^{238}Pu, ^{239}Pu, ^{242}Cm, ^{243}Cm, ^{244}Cm, ^{230}Th, ^{232}Th, ^{241}Am, and ^{237}Np. Because of the poor alpha resolution of the LS process (>300 keV), it is not readily used for isotopic analysis of multiple isotopes (e.g., ^{234}U, ^{235}U and ^{238}U). For the cleanup process, the LSC method can be used in the early investigation and the remediation phases depending on the detection limit requirements.

4.1.2.2 Photon-Electron Rejecting Alpha Liquid Scintillation

The PERALS® spectrometer combines liquid scintillation counting with electronic discrimination to reduce the background from X- and gamma-ray photons and to eliminate interferences from beta emitters in the test source. PERALS is used in conjunction with specially manufactured cocktails that combine an organic extractant (for the element of interest) with an alpha particle scintillator.

The test source must be prepared in a similar fashion as routine LSC applications; the element or radionuclide must be put into an aqueous solution quantitatively. Once into solution, the extractant scintillator extracts the radionuclide or element from the solution nearly quantitatively. An isotopic tracer of the same oxidation state as the sample can be used to verify the quantitative recovery of the target radionuclide from the sample digestion and extraction processes. Currently, extractant scintillators have been developed that permit analysis of ^{226}Ra, $^{230/232}$Th, $^{234/238}$U, ^{237}Np, $^{238/239/240}$Pu, $^{241/243}$Am, and ^{244}Cm.

The PERALS spectrometer has better alpha-particle resolution capability compared to a standard LSC. An alpha peak resolution of 300 keV is obtainable for most extractant scintillators and radionuclides. Because the alpha background (2×10^{-5} counts per second) for this system is much lower than the standard LSC, its detection capability for the alpha-emitting radionuclides is similar to that obtained from alpha spectrometry using solid state detectors. Typical detection limits for aqueous samples range from 0.0005 to 0.024 Bq/L, depending on sample volume, interferences, and counting time.

For the cleanup process, the PERALS method can be used in the early investigation and the remediation phases depending on the detection limit requirements.

4.1.2.3 Cerenkov Counting

When charged particles pass through a dielectric medium (such as water) at speeds greater than the speed of light in that medium, they will emit Cerenkov photon radiation in the direction of travel. Cerenkov radiation is emitted in the ultraviolet wavelength region. On a practical basis, Cerenkov counting is applied to radionuclides emitting beta particles having an $E_{\beta max}$ greater than 1,000 keV. The detector counting efficiency for nuclides in water increases as the $E_{\beta max}$ increases greater than 1,000 keV, ranging from about 7 percent at 1,000 keV to 70 percent at 3,520 keV.

There are certain unique advantages to using the Cerenkov radiation detection technique for the analysis of high-energy beta-emitting radionuclides. In particular, there is discrimination between detected high-energy beta particles and non-detected low-energy beta emissions. This advantage has been used to analyze ^{89}Sr ($E_{\beta max}$ = 1,488 keV and detection efficiency of about 28 percent) in the presence of ^{90}Sr ($E_{\beta max}$ = 546 keV and detector efficiency of $<$ 1 percent). Another advantage is the avoidance of using an organic scintillator and its disposal as a mixed waste and the ability to recover unaltered test sources for other purposes. In addition to water, Cerenkov radiation is produced in very acidic and alkaline solutions, solutions that may not be compatible with scintillation cocktails. Normally, an analytical method is developed so that the aqueous test source solution is prepared to avoid color quenching of Cerenkov light emissions.

The application of Cerenkov counting to environmental samples has been limited and not fully investigated. Currently, the detection methodology has been mainly used for ^{89}Sr, ^{90}Sr/Y, and ^{32}P in effluents and environmental media. For the cleanup process, the Cerenkov LSC method can be used in the early investigation and the remediation phases depending on the detection limit requirements.

4.1.3 Gamma Spectrometry

Gamma spectrometry is a sensitive method of analysis that can yield analytical data for several different nuclides in a single sample analysis. Gamma-ray emission from a radionuclide is usually preceded by the particle emissions from radioactive beta decay (either β^- or β^+) and sometimes by alpha decay. The decay leaves the nucleus in either a ground or excited state. If the nucleus is in an excited state, the decay to ground state typically is achieved by gamma emission. A nucleus may have many different energy levels through which it must pass before attaining a ground state configuration. This means that there can be one or more gamma rays emitted from an excited nucleus. Not all transitions have the same probability. If a nuclide emits a gamma ray of a specified energy each time it decays, its transition probability will be 1.0. Cobalt-60 has two gamma rays (1,173 and 1,332 keV) that are emitted, and each transition has a probability of at least 0.99. Technicum-99 emits a gamma ray at 90 keV with a probability of <0.001. Thus, it is much easier (and more practical) to detect the ^{60}Co by gamma spectrometry than the ^{99}Tc when present at very low concentrations in the environment.

Although gamma rays interact with a HPGe detector through three major mechanisms, the most important mechanism for gamma spectrometry is the photoelectric effect interaction, in which all the photon's energy is absorbed by the detector in a single event. Particularly in samples where the radionuclide concentration is very low, each gamma ray will be easily identified from other gamma rays. Each radionuclide emits gamma ray(s) at one or more energies characteristic to that nuclide, enabling the spectroscopist to identify radionuclides present in the sample uniquely. The intensity of the gamma radiation per unit time can be used to quantify the number of radionuclide atoms that have undergone decay. From this measurement, the concentration of the radionuclide (i.e., pCi/g or pCi/L) present in the sample being analyzed can be calculated.

Of the radionuclides listed in Section 1.5, the following can be determined routinely by gamma spectrometry.

- Americium-241
- Cesium-134 and 137
- Cobalt-60
- Iodine-131
- Iridium-192

It is important to note that due to the manner in which gamma-ray spectrometry is performed, "other" gamma emitters (e.g., ^{40}K, ^{7}Be, ^{228}Ac, ^{125}Sb, etc.) that are outside the scope of this document may be detected in the spectrum. These radionuclides could be from NORM or nuclear power plant (NPP) decommissioning sites. Those present from facility decommissioning will depend upon the length of time between when the plant was operating and when the samples are taken (due to half-life considerations). Some of these are listed in Table 8.

Table 8 — Possible gamma emitters that could appear in analyses due to NORM or NPP

NORM	^{40}K	^{228}Ac	^{7}Be	$^{212/214}$Pb	$^{212/214}$Bi	^{222}Rn	^{234}Th
Half-life	1.27×10^9 y	6.15 h	53.3 d	10.6 h 26.8 min	60.6 min 19.9 min	3.82 d	24.1 d
NPP*	$^{108m/110m}$Ag	$^{57/58}$Co	^{54}Mn	$^{152/154/155}$Eu	^{45}Ca	^{125}Sb	
Half-life	418 y 250 d	271 d 70.9 d	312 d	13.5 y 8.59 y 4.76 y	163 d	2.76 y	

* Also see Appendix E, *Nuclear Power Plant Decommissioning Sites*

Some of the other radionuclides may emit gamma rays upon decay, but the probability of gamma emission is very low. This means that other methodologies would be more applicable for very low concentrations of the other gamma ray-emitting isotopes.

As a nondestructive method of sample analysis, gamma spectrometry is very applicable as a screening and a radionuclide-specific methodology that can be used during all phases of the cleanup process. In most instances for screening applications, a medium-resolution, high-detection efficiency probe as part of a gamma survey unit can be used in the early investigation phase as a limited spectrometer. A common gamma probe for surveys is a NaI(Tl), with a resolution >70 keV and a dimension of 2.5 cm length by 2.5 cm diameter (or 5.1 cm long by 5.1 cm across). The response of the NaI(Tl) probe is calibrated to the radionuclide (or mixture of radionuclides) of interest and the physical dimensions (geometry) of the source of the radioactivity. The typical geometries for surveys include walls, equipment, and the ground. When evaluating a single nuclide, or two nuclides having gamma energies differing by 200 keV, survey measurements using this type of probe will quantify the gamma-emitting radionuclides in survey units (areal concentration) of a contaminated site. When there is a mixture of gamma ray-emitting radionuclides, survey measurements can be used to compare the gamma flux (total detector response over the entire energy range) from one survey area to another or to a reference background. Information on NaI detector calibrations can be found in NRC (1997).

For high-resolution, radionuclide-specific gamma spectrometry, high-purity germanium HPGe detectors are most frequently used for identifying and quantifying the gamma radiations. This type of detector, when properly shielded and collimated, also can be used as part of a portable gamma spectrometry system for performing *in situ* field surveys. *In situ* gamma-ray spectrometry has been employed by the Department of Energy for more than thirty years (Beck et al., 1972; Shebell, 2003) for measuring large areas of contaminated soil and applying computer algorithms to correlate the measured gamma spectral response to specific radionuclide soil concentrations (areal and volumetric contamination). However, soil core samples typically are collected (in the same measurement area) and analyzed to verify the soil depth profile (of the radionuclide contamination) that is used in the *in situ* software algorithms. In many cases, *in situ* gamma spectrometry has been found to be an effective field measurement tool that is quick and reduces the number of laboratory analyses that must be taken. More recently, one manufacturer has designed a portable gamma spectrometry system for measuring the average surface contamination of building structures.

Within most laboratories, a highly shielded HPGe-detector gamma-ray spectrometry system is used as a non-destructive, radionuclide-specific method. Samples of any matrix can be analyzed by this method as long as the detector is calibrated for the sample geometry and density (Z value) and radionuclide gamma energy. Typical sample volumes include 500 grams for solid matrices and one or 3.5 liters for liquid samples. Commonly used counting (measurement) times range from 6,000 to 60,000 seconds, depending on the required MDC value. In some cases, mobile laboratories have been constructed to house a highly shielded HPGe-detector gamma-ray spectrometry system for field analyses during the assessment, site inspection, and remediation phases.

4.1.4 Alpha Spectrometry

Alpha spectrometry is a radionuclide-specific method used in the laboratory to identify and quantify pure alpha-emitting radionuclides. Most laboratories employ an alpha spectrometry system as a routine detection method for the difficult-to-measure alpha-emitting radionuclides. A high-resolution alpha spectrometry system used in a laboratory consists of a semiconductor detector in a vacuum chamber electronically coupled to a multichannel analyzer operating over an energy range between 4 MeV and 8 MeV. In general, ion-implanted silicon or silicon surface barrier detectors having a diameter of ~ 25 mm and a very thin sensitive depth (typically <400 μm) are used for alpha spectrometry applications. Because the energy of the alpha particle is severely attenuated by matter, a sample must be chemically processed and the radionuclide deposited (electroplated or microprecipitation) without interferences on a metal disk or filter paper mount. The final mount is inserted into a vacuum chamber containing the semiconductor detector and analyzed in a near vacuum to avoid degradation of the alpha particle energy and alpha spectrum. Spectral resolution of alpha-particle energies more than 50 keV apart can be obtained with electrodeposition- and microprecipitation-mounting techniques.

Alpha spectrometry as a radionuclide-specific method can be used during the early investigation and remediation phases. In most cases, alpha spectrometry is chosen when the historical source term information indicates the likely presence of the alpha-emitting radionuclides or when alpha screening has indicated elevated alpha levels. For routine low-level environmental radionuclide analyses, the typical sample processing time for most methods is one day for sample processing and one day for counting. The typical minimum detectable activity obtained in a 60,000 second measurement is ~ 0.03 pCi or 0.001 Bq per sample for water and soil samples. The method is used for isotopic analysis of ^{234}U, ^{235}U, and ^{238}U; ^{210}Po, ^{223}Ra, ^{224}Ra, and ^{226}Ra; ^{237}Np, ^{238}Pu, and ^{239}Pu; ^{241}Am, ^{242}Cm, and ^{244}Cm; and ^{228}Th, ^{230}Th, and ^{232}Th.

4.2 Atom-Counting Methods

Atom-counting methods are grouped within the special methodologies (Section 2.3) and are used in the analysis of certain longer-lived radionuclides (e.g., ^{232}Th, ^{235}U, and ^{238}U) when very low activity levels are encountered or when isotopic mass ratios are required. Atom-counting methods are confined to laboratory operations and are not typically used in the field. The application of the atom-counting methods would be for characterizing the radioactive source by isotope or element during the characterization and remediation phases.

The two-atom counting methods discussed in this document include kinetic phosphorimetry analysis (KPA) and mass spectrometry. Mass spectrometric methods can be used in the characterization phase to determine if the isotopic ratio (e.g., ^{240}Pu/^{239}Pu mass ratio) is a signature of the source-term contamination. Highly sensitive mass-spectrometric measurement of the ratio of ^{238}U:^{235}U is used routinely to determine whether uranium is of natural origin or if it may be contaminated with depleted uranium or enriched uranium. In some cases, a highly sensitive elemental analysis (such as uranium and thorium) rather than an isotopic analysis would be more applicable, e.g., the non-mass spectrometric atom-counting method of KPA. Sample-processing time usually is longer and much more expensive for mass spectrometric analyses compared to KPA. Therefore, the sample analysis by mass spectrometry would only be used in those phases when isotopic identification or low-activity measurements for very long-lived radionuclides are required.

4.2.1 Kinetic Phosphorimetry Analysis

Kinetic phosphorimetry analysis is based on the measurement of ionic phosphorescence of a species taken at selected time intervals after excitation. The intensity of the phosphorescence is related to the concentration of the analyte. KPA does not measure radioactive emissions but UV-V as light emitted from a sample solution containing certain molecular species.

The analyte in the sample solution is excited by using a laser (commonly a nitrogen laser is used) of energy equal to or greater than the excitation transition energy. A short laser pulse (on the order of nanoseconds) will initiate a measurement cycle. Phosphorescence emission is measured at right angles to the excitation wavelength, and delayed between 0.0001 and 10 seconds, from the incident excitation.

Because KPA is an outer electronic orbital phenomenon (that is, it involves valence shell electron orbitals and higher energy orbitals), the valence state of the analyte can have a significant effect on the analysis. It is also important to note that the phosphorescent light emission is independent of the specific isotopes of the element present in the sample. All isotopes of the element will yield the same phosphorescence as long as they are in the same oxidation state. For example, U^{+4} is not sensitive to the process, but U(VI) is sensitive. Thus, a sample to be analyzed by KPA for uranium would need to have all the uranium oxidized to U(VI) using an oxidant such as nitric or perchloric acid.

KPA has been applied to uranium and lanthanide analyses in the range of 0.01 ppb (~ 0.2 mBq/L) to percent by weight composition of materials. The method lends itself to the analysis of samples with significant uranium content (ores, mill tailings, soils contaminated with spilled uranium solutions, etc.) as opposed to background uranium measurements (seawater, river sediments etc.).

4.2.2 Mass Spectrometry

Detection of elements by mass spectrometry (MS) does not depend on the atoms' radioactive or chemical properties. It depends only on the mass of the nucleus and the ionic charge of the atom when introduced into the mass spectrometer. There are a variety of methods by which samples may be introduced into the detection system. These methods become part of the hyphenated name with MS.

Generally, MS techniques have better quantification capabilities than radioactive decay-emission detection techniques for low-activity (< 0.1 Bq) samples of radionuclides with half-lives greater than about 100 years. Decay-emission measurement techniques have trouble distinguishing background decay emissions per unit time from low-activity samples. Table 9 identifies, for a given concentration, the number of atoms present for radionuclides with a wide range of half-lives. Note that the same activity has vastly differing numbers of atoms, but the activity concentrations are the same.

TABLE 9 — Number of atoms of radionuclides with activity of 0.1 Bq

Radionuclide	Half-life (years)	Atoms	Concentration pCi/L	Concentration moles/L
^{210}Bi	1.37×10^{-2}	6.23×10^{4}	2.7	1.03×10^{-19}
^{90}Sr	2.91×10^{1}	1.33×10^{8}	2.7	2.21×10^{-16}
^{243}Am	7.37×10^{3}	3.35×10^{10}	2.7	5.56×10^{-14}
^{99}Tc	2.13×10^{5}	9.68×10^{11}	2.7	1.60×10^{-12}
^{232}Th	1.4×10^{10}	6.36×10^{16}	2.7	1.06×10^{-7}

As with most highly sensitive analyses, mass spectrometry methods require sample preparation/ digestion and chemical isolation and purification prior to injecting the test source into the mass spectrometer. In addition, special highly purified reagents (e.g., nitric acid) and benchware (beakers, vials, etc.) must be used to avoid contamination of the sample with minute trace quantities of the target element or radionuclide. Depending on the element or target radionuclide, the sample preparation and chemical processing may be conducted in a clean room to prevent contamination from ambient airborne contaminants. A few of the more commonly used mass spectrometric methods are identified below.

4.2.2.1 Inductively Coupled Plasma-Mass Spectrometry

ICP-MS is a hybrid technique for elemental analysis. It is the connection of an inductively coupled plasma (ICP) unit for measuring emission lines of excited atoms with a mass spectrometer (MS). The method uses the ICP portion to introduce samples as ionized gasses into the mass spectrometer, which sorts out these ions based on their charge to mass ratio. The integrated instrument has the following basic components:

- Sample introduction system
- Torch
- Interface
- Vacuum system
- Lens
- Quadrupole
- Detector

Most samples that are analyzed by ICP-MS are liquids. These samples would have undergone digestion in aqueous media in exactly the same way as any sample prepared for radioactivity measurements but with less emphasis on major elemental interferences. The sample is introduced to an argon plasma torch using a nebulizer spray chamber (analogous to the type used in an atomic absorption spectrometer). The argon plasma transforms all constituents to ionized elements. The ions are passed through a vacuum interface through a focusing lens and into the quadrupole mass separator. The ions are focused onto a detector (similar to a PMT) that counts individual events at a particular charge-to-mass ratio. Commercial instruments have the capability of scanning the mass range from 1 to 240 atomic mass units (amu) in a few tenths of a second and achieving detection limits in the 0.1 to 1 ppb range during that time. Solid and gaseous samples can also be analyzed directly by altering the sample introduction format. As with all other methods of analysis that require sample preparation, this method can be affected by incomplete sample dissolution.

The benefit of this technique is that it counts atoms present in the sample as opposed to waiting for decay events to occur. Thus it has a specific advantage over decay-particle-detection techniques for long-lived isotopes, i.e., signal accumulation time is much less. Another advantage is that for isotopes like ^{239}Pu and ^{240}Pu (which have alpha particle energies that are almost exactly the same), the mass separation can be used effectively to identify and quantify these isotopes separately.

This technique has potential isobaric interferences resulting from combinations of abundant ions in the mass spectrometer. An instance of isobaric interference comes from a combination of ^{58}Ni and ^{1}H (noted as “Ni-58:H” in the Appendix D table) as a combined ion yielding a signal at mass number

59. For example, if ^{59}Ni were being analyzed from reactor-coolant piping, the ^{58}Ni would be present in large mass amounts from the steel, and the ^{1}H would come from the water matrix. Thus, an interference correction must be applied.

This technique also has great utility in assessing the isotopic ratios of certain elements that can determine what the sample history has been. This technique of isotopic ratios can also be used for a trace element technique known as isotopic dilution analysis (IDA).

4.2.2.2 Thermal Ionization Mass Spectrometry

Thermal ionization mass spectrometry (TIMS) ionizes an element by heating a metal filament on which the target nuclide has been electroplated. TIMS has been used to analyze ^{235}U, ^{238}U, ^{239}Pu, and ^{240}Pu in a variety of environmental and bioassay matrices. A detection limit of about 6 µBq per sample is typical for ^{239}Pu. TIMS and quadrupole ICP-MS have similar detection limits for uranium—about 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). TIMS is able to measure ^{238}U/^{235}U ratios in ranges between 138 and 220 for levels between 25 to more than 350 ng/kg.

4.2.2.3 Accelerator Mass Spectrometry

Accelerator mass spectrometry (AMS) is a sensitive analytical technique that uses an ion accelerator and a beam transport system to provide different levels of mass and charge analysis, ultimately counting individual ionized atoms. The low range sensitivity of AMS is not encumbered by the half-life of the isotope being measured, because the atoms, not their radioactive emissions, are counted. Isobaric identification is possible because AMS is unaffected by most background mass peaks, because molecular ions are destroyed in the transport of the ions through the instrument. A basic system is composed of the following:

- A sample holder;
- An ionizing source projected onto the sample;
- An injection system that includes beam transport, and beam analysis equipment;
- A tandem accelerators; and
- A detector (gas ionization counters are commonly used).

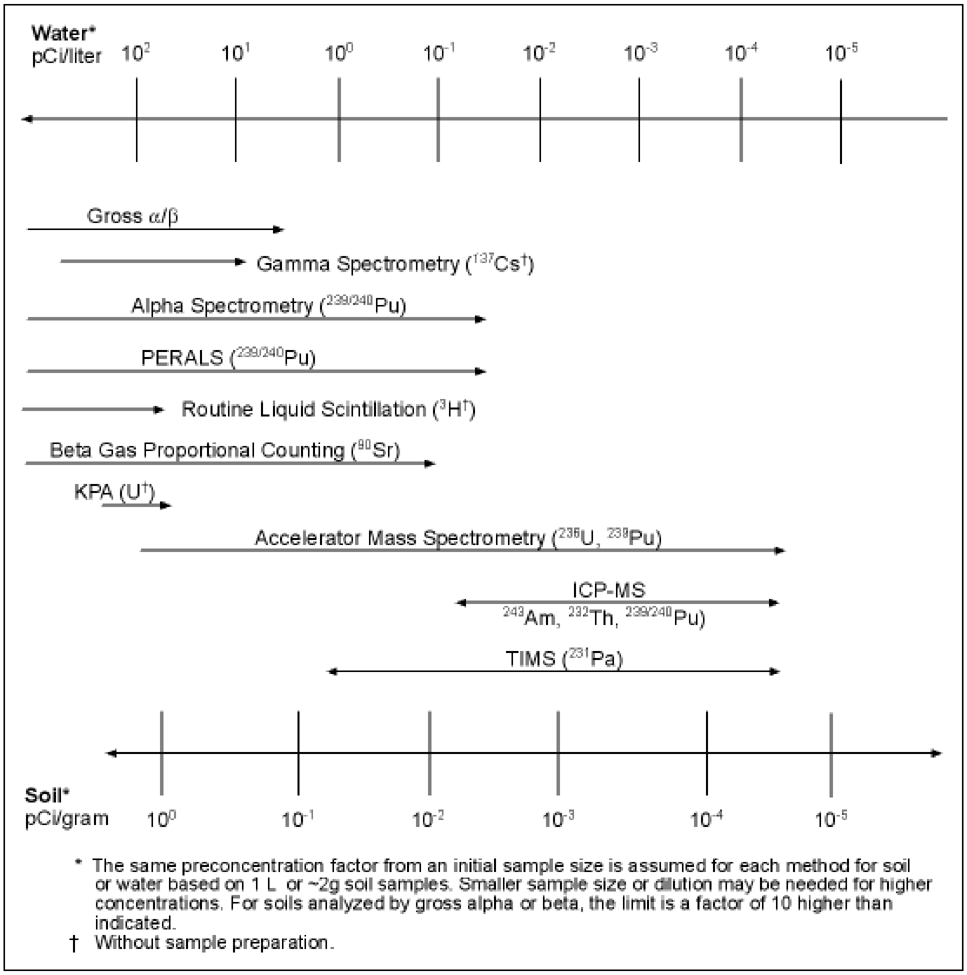
The sample holder is a metal cup (aluminum and copper have been used) in which the solid sample is held. An ion beam is then directed at the sample to cause it to sputter. Sputter sources (e.g., heated cesium metal producing Cs^+) cause the sample to form negative ions. Ions produced in the sample from the sputter source impact undergo energy and mass analysis before being injected into the accelerator. The accelerator can have low and high energy tubes with a thin foil or gas stripper placed in the high-voltage terminal between the low- and high-energy tubes to convert negative ions to positive ions. The positive ions are then put through a second mass analyzer before being focused on a gas ionization-type detector. The measured pulse height from the detector is directly related to the number of produced electrons in the detector. The number of electrons is a measure of the energy the ion lost inside the active detector space. These detectors have two advantages: they are not subject to radiation damage and can be adjusted for varying atomic units.

The benefit of AMS analysis for long-lived isotopes is that instead of counting random events from large samples over the course of days, milligram samples can be analyzed in several minutes. The sensitivity of AMS is five to six orders of magnitude below radioactivity measurements for these long-lived isotopes. Among the radioisotopes that can be analyzed by this method are ^{129}I, ^{14}C, $^{59/63}$Ni, ^{3}H, $^{7/10}$Be, ^{41}Ca, ^{36}Cl, ^{90}Sr, ^{99}Tc, ^{129}I, ^{239}Pu, ^{240}Pu, and ^{236}U. Some disadvantages of this method are:

- Not all atoms can be analyzed because they do not all produce significantly long-lived negative ions;
- The final analyte form must be a solid that is formed after sample treatment;
- The instrumentation is currently very expensive;
- The equipment takes up a considerable amount of floor space (9 – 185 m^2, depending upon the number and types of isotopes being analyzed); and
- AMS can suffer from isobaric interferences similar to that of ICP-MS.

4.2.3 Summary of Analytical Methodologies, Minimum Detectable Concentrations, and Instrument Types

Figure 2 displays the range of concentrations that the different radioanalytical methods described above generally are capable of achieving. Note that each methodology will have a specific MDC for each of the different radionuclides.



* The same preconcentration factor from an initial sample size is assumed for each method for soil or water based on 1 L or ~2g soil samples. Smaller sample size or dilution may be needed for higher concentrations. For soils analyzed by gross alpha or beta, the limit is a factor of 10 higher than indicated.

† Without sample preparation.

FIGURE 2 — Nominal minimum detectable concentration for different radiation-detection and atom-counting methods

Table 10 summarizes the applicability of the analytical methodologies described in this section to various radionuclides.

TABLE 10 — Analytical methods applicable to each radionuclide

	Screening				Routine Radiochemical							Special		
Method / Nuclide	GP α	LSC β	GP β	GG††	GS†	GP	AS	KPA	LS	PERALS®	Cerenkov	ICP-MS	TIMS	AMS
^{241}Am	●			●	○	○	●			○			○	○
^{243}Am	●					○	●			○			○	○
^{210}Bi		○	●			●			○		○			
^{14}C		●				○			●				○	○
$^{242/243/244}$Cm	●						●						○	○
^{134}Cs		○	●	●	●									
^{137}Cs		○	●	●	●									
^{60}Co		○	●	●	●									
^{55}Fe		●			○				●					
^{3}H		●							●					○
^{125}I				○	●				○					
^{129}I		●		○	○	○			●			●	●	●
^{131}I		●	●	●	●	●			○					
^{192}Ir			○	●	●	○								
^{237}Np	●			○			●					○	○	○
^{59}Ni				○	○				●					
^{63}Ni		●				○			●					○
^{32}P		○	●			○			●		○			
^{210}Pb		○	●	○	○	●			○					
^{210}Po	●						●							
^{238}Pu	●						●			○				
^{239}Pu	●						●			○*		○	○	○
^{240}Pu	●						●			○*		○	○	○
^{241}Pu		●							●					
^{226}Ra §	●			○	○	●	○		○	○				
^{228}Ra			●	●	●	●			○					
^{89}Sr		○	●			●					○			
^{90}Sr		○	●			●					○			
^{35}S		●	○			○			○					
^{99}Tc		●	○			○			●			○	○	○
^{227}Th	●			○			●			○				
^{228}Th	●			○	●		●			○				
^{230}Th	●						●			○		○	○	○
^{232}Th	●			○	●		●			○		●	○	○
^{234}U	●						●			○		○	○	○
^{235}U	●			○	●		●			○		○	○	○
^{238}U	●			○	●		●			○		●	○	○
U, total	●			○		○	●	●		○		●	○	○

Notes: ○ Applicable technique ● Most common technique

GPC: gas proportional counting; LS: liquid scintillation counting; GG: gross gamma counting using NaI(Tl) and Ge detectors; GS: gamma spectrometry; AS: alpha spectrometry; LS: liquid scintillation; KPA: kinetic phosphorimetry analysis; ICP-MS: inductively coupled plasma mass spectrometry; TIMS: thermal ionization mass spectrometry; AMS: accelerator mass spectrometry.

* $^{239/240}$Pu cannot be resolved by this technique, and the reported results are the sum of the activities of the two isotopes.

† GS also includes low-energy gamma- and X-ray analysis

§ ^{226}Ra is commonly analyzed by radon emanation (see Section 5.13)

†† Gross gamma screening for environmental levels of ^{226}Ra, ^{228}Ra, ^{210}Pb, U, Th, and transuranics applies only to solid samples.

5 Chemical and Physical Properties for Selected Radionuclides

The radionuclides in this document represent the most common or significant (in terms of radiation-health effects) likely to be encountered at a large cleanup site. For example, the radionuclides found at NORM sites are radium, uranium, thorium, and their decay products. If wastes from processing ores containing these materials are causing elevated radioactivity, it is likely that the isotopes listed here as NORM would be responsible for that elevated activity. Similarly, a DOE site decommissioning may contain the radionuclides in the transuranic family (e.g., plutonium and americium). Other radionuclides may be present (e.g., ^{40}K, ^{7}Be, ^{228}Ac, etc.), but their quantity, concentration, or dose consequence will be negligible compared to those described here.

This section provides a brief description of the chemical separation and analytical techniques for each radionuclide. Appendix D contains tables for each element that provide technical information regarding radionuclide detection limits by specific methodologies (page 80).

5.1 Americium

Americium has no naturally occurring isotopes. It is produced synthetically by neutron bombardment of ^{238}U or ^{239}Pu followed by beta decay of the unstable intermediates. Americium-241 ($t_{½}$ = 432 y) is found in military wastes and can be extracted from reactor wastes. Some industrial ionization sources also contain americium. Kilogram quantities of ^{241}Am are available, but only 10- to 100-g quantities of ^{243}Am ($t_{½} \approx$ 7,371 y) are prepared. Low-energy gamma emission from ^{241}Am is used to measure the thickness of metal sheets and metal coatings, the degree of soil compaction, and 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.

Am^{+3} is the oxidation state that would be found in environmental samples. Although other oxidation states exist, they are not chemically stable and are reduced or oxidized to the +3 state in solution. Free radicals produced by radiolysis of water by alpha particles reduce the higher states spontaneously to Am^{+3}. The +3 oxidation state exists as $Am(OH)_3$ in alkaline solution. Simple tetravalent americium is unstable in mineral acid solutions, disproportionating rapidly to produce Am^{+3} and AmO_2^{+1} [Am(V)] in nitric and perchloric acid solutions. Conversely, dissociation of $Am(OH)_4$ or AmO_2 (both Am^{+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.

Americium is generally thought to be adsorbed by soils at pH values found in the environment. Complexation of Am^{+3} by naturally occurring ligands (humic and fulvic acids), however, would be expected to strongly reduce its adsorption.

Laboratory analysis of americium involves separation from other transuranic elements by methods of ion exchange, solvent extraction/extraction chromotography, or precipitation. Gamma spectrometry can be used for analysis of ^{241}Am when in sufficient quantity, while both ^{241}Am and ^{243}Am can be determined by alpha spectrometry.

Am-243 has been used as a monitor for ^{241}Am yield when it is known that no ^{243}Am is present in the sample. Cm-243 has been used as a surrogate yield monitor as well. No other radionuclides are routinely used as yield monitors. Gravimetric separation of americium for alpha analysis is achieved using either neodymium or lanthanum fluoride as a carrier (actually a co-precipitant).

5.2 Bismuth

Bismuth has the highest atomic mass of any stable element. It has only one stable isotope, ^{209}Bi. Bi-210 ($t_{½} \approx 5.0$ d) is part of the decay chain of ^{238}U, as is its immediate precursor, ^{210}Pb, which has a half-life of 22.2 years. In many types of environmental samples, these radionuclides may be found in secular equilibrium with each other. However, due to some differences in solubility and complexation, the secular equilibrium connection may be broken. This means that some or all of the ^{210}Bi present may be unsupported (see Appendix B). Thus, the sampling conditions, time to start chemical analysis, and time to complete the analysis all become important in the determination of ^{210}Bi.

Because ^{210}Bi is a beta emitter but not a strong gamma emitter, it is most frequently measured either by GP counting or by liquid scintillation. In either case, chemical separation is required first. This is routinely accomplished through ion exchange and precipitation. Bismuth has only one oxidation state (+3), making its sample processing relatively straightforward.

Chemical yield of bismuth can be monitored using stable bismuth carrier and determining it either gravimetrically as bismuth oxychloride or spectrophotometrically using atomic absorption or colorimetric techniques.

5.3 Carbon

The chemistry of carbon compounds and their occurrence are too extensive to be summarized here. Fortunately, only one isotope of carbon, ^{14}C ($t_{½} \approx 5{,}720$ y, beta emission), is significant for analysis in environmental samples. However, ^{14}C is incorporated into many organic compounds as a tracer for research. Once the ^{14}C is covalently bound in a molecule, its chemistry follows that of the molecule and not of carbon, unless the organic molecule is destroyed. In those instances it would most likely be converted to carbon dioxide. Therefore, in those instances in which it is suspected that organic compounds may be present, sampling methods should not be employed that could possibly exclude any ^{14}C compounds. As mentioned in Section 3.2.1, samples to be analyzed for ^{14}C should not be preserved in acid. Addition of acid could cause oxidation of any organic material containing ^{14}C, which would be subsequently expelled as CO_2 gas. Additionally, the sample analysis regime should include oxidation of the parent molecule to carbon dioxide. This will depend on whether or not multiple compounds may be present that contain ^{14}C. Where more than one type of compound may be present, sample oxidation is required. The CO_2 is captured subsequently and prepared for liquid scintillation analysis. The liquid sample prepared in this fashion may also be used for ICP-MS analysis. AMS has become a feasible technique for carbon, especially for solid samples.

No other significantly long-lived radionuclides of ^{14}C exist. Thus, a radiotracer yield monitor is not available, and 100 percent recovery would be assumed. Certain methods that use a carbon carrier and determine the original carbon content of the sample can realize specific recovery data. This is generally done using sample oxidation and subsequent $BaCO_3$ gravimetry.

5.4 Cesium

Cesium has two principal isotopes that are discussed in this document, ^{137}Cs ($t_{½} \approx 30$ y) and ^{134}Cs ($t_{½} \approx 2.1$ y). Cesium is in the IA group of the Periodic Table, which means that it is present in samples either as the metal or in the +1 oxidation state. The metal has a melting point of 28 °C and oxidizes rapidly in air to yield Cs_2O. The chemistry of cesium is relatively simple. It forms weak complex ions in aqueous media and can be separated/concentrated by ion exchange chromatography using a cation resin. Cesium does not form any anionic complexes, and this can be used as an effective separation tool if other radionuclides that do form anionic complexes are present. Cesium can move very rapidly in ground water. Cesium is still found in a variety of environmental matrices as a result of nuclear fallout and nuclear power plant discharges. The concentrations at which these isotopes are being found is decreasing overall.

Cesium-137 is used as a check source for a variety of different instruments and is readily available as a radioisotope. Although present as a solid material in such sources, if the source is damaged, leakage of the cesium is likely due to its solubility and volatility.

In most cases chemical separation from other radionuclides is not performed. The two radionuclides of cesium are usually measured directly by gamma ray spectrometry, whether the sample is soil or water. There is no significant concern for decay correction because of the long half-lives of the two isotopes.

One significant precaution should be noted in the analysis of ^{134}Cs. Results may be biased low due to gamma-ray coincidence summing effects when using gamma-ray spectrometry. This effect may be accounted for by calibration correction, increasing sample-to-detector distance, or direct calibration with a ^{134}Cs source.

A chemical yield monitor for cesium is not generally used because it is almost always determined without chemical separation by gamma spectrometry.

5.5 Cobalt

The principal radioisotopes of cobalt (with their half-lives) are ^{57}Co ($t_{½} \approx 272$ d), ^{58}Co ($t_{½} \approx 71$ d), and ^{60}Co ($t_{½} \approx 5.27$ y). All these isotopes may be found in effluents and components of nuclear power plants. The ^{60}Co isotope is used to sterilize food by irradiation and in cancer treatments as a radiation source. Thus there are significant quantities of ^{60}Co available. Isotopes 57 and 58 can be determined by X-ray as well as gamma spectrometry. The ^{60}Co isotope is easily determined by gamma spectrometry because no significant decay of the isotope occurs during sampling and analysis, it has two gamma rays with energies high enough that they are not attenuated by sample density, and each decay of the isotope leads to each of the gamma rays being produced.

Cobalt only has one oxidation state (+2) to be concerned with in environmental samples. It is easily solubilized by either hydrochloric or nitric acid and will form both positive and negative complexes in aqueous solutions with a variety of anions. For this reason, it is easily separated from other metal ions by ion-exchange chromatography using either a cation or anion resin. Cobalt forms very insoluble CoS in environments where sulfide ions are present. Because some water samples will have sulfide ions present due to the presence of decaying organic materials, some cobalt can be lost to container adsorption or inadvertent decantation. Potentially high bias can occur if sedimentation occurs while the sample is being counted directly on a gamma ray spectrometer. Care must be taken with these samples. In addition, if the sample is processed so that the cobalt is chemically separated, special techniques to dissolve the CoS may be required.

All three isotopes of cobalt decay by gamma emission. For this reason, these nuclides are generally determined without chemical separation when they are present in significant activity. A chemical yield monitor is not generally used, as no analyte separation is involved using gamma ray spectrometry.

5.6 Hydrogen (Tritium)

Tritium (^{3}H; $t_{½} \approx 12.3$ y) is found most commonly in water. The only radioactive isotope of hydrogen, its chemistry is that of the hydrogen ion. Once in the environment, most compounds that contain tritium will undergo oxidation to water. Tritium has been incorporated into a variety of compounds in which it is covalently bound. It has a great utility as a chemical tracer on organic and specific bio-molecules when it is incorporated into a non-labile portion of the molecule. Tritium containing compounds are used in liquid crystal devices (LCDs) and for illumination in certain types of signs.

The beta particle emitted by the tritium atom is of very low energy. Liquid scintillation is by far the most commonly used technique of analysis for tritium in water or solid samples. Both atomic mass spectrometry and ICP-MS have been used for its analysis (Chiarappa-Zucca, 2002; Demange, 2002). One of the interesting characteristics of tritium in the environment is that it will migrate easily. Because it is chemically identical to hydrogen, it can exchange freely with hydrogen atoms in water molecules. This means that tritium can have countercurrent flow in aquifers and other ground waters. It also means that it will diffuse rapidly.

Its characteristic of being easily exchangeable with water is also a positive aspect because it can be easily separated from other materials based on the physical properties of water. Thus, if tritium analysis of a soil sample is necessary, the water can be separated by filtration, distillation, or freeze-drying, and the resultant water (free of everything else) can be analyzed directly for tritium.

Tritium naturally exists in the environment as a result of cosmic ray interaction with atoms of the upper atmosphere. It also exists as a result of atmospheric testing of nuclear weapons and discharges from nuclear power plants and other facilities where tritium is produced. The concentration in the environment due to natural sources is less than 50 pCi/L (1.8 Bq/L).

There are underground aquifers that have been isolated from the environment for very long periods of time. Water taken from such a location will have much lower concentrations of tritium (sometimes referred to as “dead water”) than those water sources that can exchange with the environment, because of tritium’s relatively short half-life.

Analysis for tritium does not involve the use of a chemical yield monitor. Because the tritium in the samples is part of a water molecule, water is the “preservative”: ensuring that no tritium is lost in processing.

5.7 Iodine

Iodine belongs to the halogen family (Periodic Table Group VII) of elements and can exist in seven different oxidation states. Its most common states are -1, +1, (V), and (VII). Iodine does not exist in the environment in its elemental form. Elemental iodine sublimes at ambient temperatures.

All iodine radionuclides are produced as a result of nuclear fission (e.g., ^{129}I, $t_{½} \approx 1.57 \times 10^7$ y and ^{131}I, $t_{½} \approx 8.1$ d) or cyclotron production (e.g., ^{125}I, $t_{½} \approx 59.4$ d) of specific isotopes. Very low levels of ^{129}I exist in the environment as a result of spontaneous fission. However, this concentration is well below that which would be determined by routine radiochemical analysis (Cecil et al., 2003). Isotopes of ^{125}I and ^{131}I are routinely produced for radio-therapeutic purposes, and are commonly found as contaminants in medical wastes and wastewater. Iodine-129 is a fission product. Its low-energy beta and gamma emissions make it difficult to determine in most matrices without some form of chemical separation.

The chemistry of iodine can create significant challenges to the sampler and analyst. The multivalent nature of iodine can create problems with sample storage and transit prior to analysis. Although the elemental state does not exist in the environment, it can be formed as a result of other chemicals in the sample (e.g., oxygen). Thus, some iodine may be lost as a result of volatilization unless steps are taken to ensure all iodine is converted to the I^- ion immediately following sampling.

Analysis of iodine is somewhat different than with most other radionuclides, because it is the complex former (i.e., the ligand) rather than the central ion (like the metallic radionuclides, sulfur or phosphorus) of a molecule. Anion exchange resin is commonly used to concentrate ^{131}I (iodide) from water and milk samples. Solvent extraction of iodine as I_2 has been used successfully to separate iodine from other radionuclides. However, this method means that there is a likelihood of loss of iodine as a result of volatilization. Thus, the most effective means of separating iodine from other radionuclides generally is through use of an iodide carrier followed by oxidation reduction and precipitation reactions specific to iodine.

Each nuclide of iodine may be analyzed by a different method. Iodine-131 can be determined in liquid samples, directly, by its characteristic gamma ray at 364 keV. Analysis of environmental samples is very time dependant due to the 8-day half-life of ^{131}I. It is important for analysis of this isotope to know the time period of sample collection (start to stop), as well as the times to final separation of iodine (if performed), and of the total sample counting interval. All these factor into the calculation of activity.

Iodine-125 decays by electron capture and emits characteristic X-rays at 28.6 keV (usually analyzed with a low-energy germanium detector). Because of its long half-life and low emission energies, ^{129}I is most easily analyzed by liquid scintillation. Chemical yield for iodine can be determined gravimetrically using iodine carrier and precipitating quantitatively as PdI_4, AgI, and CuI.

5.8 Iridium

Iridium is one of the noble metals. It is in Group VIII of the Periodic Table and has a very low natural abundance in the Earth's crust. Heating any iridium compounds above 200 °C in air will yield the metal (the melting point of the metal is 2,443 °C). Iridium can form halogenated compounds in the +1, +3, and +4 oxidation states. However, the most stable form of this element is as the metal.

Iridium has two stable isotopes, ^{191}Ir and ^{193}Ir. Iridium-192 ($t_{½} \approx 73.8$ d) is formed as a result of neutron irradiation of the ^{191}Ir isotope. It undergoes radioactive decay by both β^-(95%) and β^+ (5%). It is principally a low-energy gamma and X-ray emitter. These characteristics make it easily identifiable without any chemical separation.

Iridium-192 is used principally for radiography of steel components and brachytherapy (implanting radioisotope seeds within or very close to tumors). The iridium, used as a point source, is in the shape of a small needle (sometimes called a "seed") and is only several millimeters in each dimension. These sources are on the order of 1-500 Ci each. The seeds are shipped in individual containers for shielding as the metal. It is unlikely for the seed to disperse easily in the environment due to the extreme inertness of the iridium metal. Dispersion of powdered material by an explosive device would yield contamination over a large area, that would settle rapidly (due to its high density of 22.5 g/cm^3) and remain relatively fixed in place due to its inertness.

The most effective technique of analysis would be by HPGe (high-purity germanium) detection. However because the emitted gamma rays are of low energy, precautions should be taken with sample thickness to avoid self-shielding. Dissolution of a sample containing iridium, using normal acid digestion, would leave the iridium behind in the residue. This might be one method of separating the iridium from almost all other radionuclides.

5.9 Lead

Lead has several naturally occurring radionuclides because it forms part of the naturally occurring decay chains of all the thorium and uranium isotopes. The isotope of interest in NORM waste is ^{210}Pb ($t_{½} \approx 22.2$ y), which decays principally by low-energy beta-gamma emission. The two other isotopes commonly associated with this type of sample would be ^{212}Pb ($t_{½} \approx 11$ h) and ^{214}Pb ($t_{½} \approx$ 27 min). These isotopes are usually determined in conjunction with radium/radon radioactive equilibria because their activity builds up so quickly (due to their short half-lives) after separation of these radionuclides.

Lead may be found in one of three oxidation states: 0, +2, or +4. The +2 state is more commonly encountered in water and soil samples. Lead nitrates, perchlorates, fluorides, chlorides (in hot water), and acetates are all soluble. Lead forms very stable complexes with chelates such as ethylenediamine tetraacetate (EDTA) and amines, but it is only weakly associated in complexes with inorganic ligands. Thus in solutions of concentrated acids, it is present as a cation and can be easily removed by cation exchange.

Lead forms very insoluble salts with hydroxide, sulfate, and sulfide. However, it does form extremely stable compounds in organic solvents with sulfur-based organic ligands such as dithiocarbamate and diphenylthiocarbazone.

In most samples that are analyzed for lead radionuclides, the amount of stable lead is very small and lead carrier is often added to determine the yield. However, it may be necessary to assess the samples' stable lead concentration prior to performing radiochemical lead analysis.

It should be noted that freshly prepared lead and lead salts from ore may have measurable quantities of ^{210}Pb in it. Thus the material used as carrier for lead should be evaluated for its ^{210}Pb content. For low-level detection of gamma rays with germanium detectors, the preferred type of lead shielding to use is "old lead" (usually more than 100 years from when it was produced from an ore). The ^{210}Pb has undergone about four half-lives at that time and will yield low background radiation.

The relatively long half-life for ^{210}Pb, and the low energy of its decay particles makes it difficult to determine at very low levels. One method of analysis uses the in-growth of the first progeny of lead ^{210}Bi ($t_{½} \approx 5.0$ d). Lead is then determined based on the activity of the shorter lived bismuth isotope determined at a fixed time after separation of lead from bismuth in HCl solution. Bismuth precipitates as an insoluble oxychloride in hot water and lead chloride remains in solution.

5.10 Nickel

The two isotopes of nickel addressed in this document, ^{59}Ni ($t_{½} \approx 76{,}400$ y) and ^{63}Ni ($t_{½} \approx 100$ y) are both formed as a consequence of neutron activation of elemental nickel. Nickel is used as an alloying element in stainless steel, Inconel®, and other components used in nuclear reactors. The radionuclides can be formed as a result of direct irradiation of reactor components by neutrons, or corrosion products transported through the reactor core can become radioactive.

Neither radioisotope of nickel produces a gamma ray when it undergoes decay. The electron capture decay of ^{59}Ni yields a low-energy X-ray from cobalt of 6.93 keV, while the energy of the β^- decay of ^{63}Ni is of very low energy (0.06 MeV). Both of these circumstances necessitate the chemical separation of nickel from other radionuclides before they can be analytically determined.

Nickel has only one oxidation state that is seen under normal aqueous chemistry conditions; +2. It can be oxidized to the +3 or +4 state by very strong oxidants. Both of these are unstable in solution and revert to the +2 oxidation state. The soluble salts of nickel are the chlorides, fluorides, sulfates, nitrates, perchlorates, and iodides. Nickel sulfide and nickel hydroxide are very insoluble compounds of nickel. The sulfide, upon extended exposure to an aerated, basic solution, will form Ni(OH)S (one of the few, stable, +3 compounds), which is extremely difficult to redissolve. The hydroxide is a light-green gelatinous precipitate that can act as a scavenger for other radionuclides. However, its gelatinous nature makes it extremely difficult to filter. It is therefore seldom used, and care should be taken to avoid its formation in aqueous solutions.

Nickel analysis is aided by its favorable complexation with ammonia and amines. This feature provides the principal means of chemical separation of nickel from its other transition metal counterparts, as well as the transuranics. In ammoniacal solution between pH 6-9, nickel is very soluble, while most other metals precipitate as the hydroxide. Nickel also will form complexes with amines in organic phases making solvent extraction an attractive means of separation.

Nickel forms very weak complexes with chloride and fluoride, which can be used to separate it from other transition metals by anion exchange chromatography. Chemical yield determination for nickel can be performed gravimetrically using the nickel dimethylglyoxime precipitate or by atomic absorption analysis.

5.11 Phosphorus

Phosphorus has two radionuclides that are used routinely, ^{32}P ($t_{½} \approx$ 14 d) and ^{33}P ($t_{½} \approx$ 25 d). Both isotopes usually are produced by a particle accelerator nuclear reaction on a sulfur target. Both nuclides emit only beta particles, so the two most common methodologies of analysis are liquid scintillation and gas proportional counting. All other isotopes of phosphorus are much shorter lived ($t_{½} <$ 3 min) and not commonly used.

The radiochemistry of phosphorus is somewhat different from the other radionuclides. Phosphorus is found in the environment, principally in the orthophosphate (PO_4^{3-}) form. Phosphorus, like carbon, is non-metallic and is usually found covalently bound into many different types of compounds. In these forms, it does not react as orthophosphate but as the molecule of which it is a part. As with carbon, phosphorus must be determined either from the chemistry of the molecule it is contained in, or the material must be digested so that phosphorus converts to its principal inorganic form, orthophosphate. If chemical separation is performed, the yield for phosphorus analysis would be determined gravimetrically using a precipitate such as barium phosphate. Analysis for ^{32}P can be done directly from many types of biological matrices if no other radionuclides are present, because of the high beta particle energy (1.71 MeV) it emits.

5.12 Plutonium

Plutonium has no naturally occurring radionuclides. Its presence in the environment is due almost entirely to anthropogenic activities (a very small quantity is present as a result of naturally occurring spontaneous fission). Plutonium isotopes discussed in this document are formed as a result of neutron capture of uranium isotopes that are in the vicinity of other, fissioning, uranium isotopes. The fuel in nuclear reactors can produce several different isotopes of plutonium due to multiple neutron capture by the same nuclide. Thus the activation of ^{238}U leads to the formation of ^{239}U, which decays through ^{239}Np to ^{239}Pu. Because the half-life of ^{239}Pu is 2.4×10^4 years, it can capture additional neutrons while in the reactor core. In this manner of multiple neutron captures, ^{240}Pu, and ^{241}Pu, can be formed. Some of the ^{235}U also undergoes similar multiple neutron capture and ^{238}Pu can be formed.

Other radionuclides, like $^{236/237}Pu$, are accelerator produced and are used as tracers in the analysis of the reactor produced plutonium isotopes.

Plutonium can have oxidation states of +3, +4, (V), and (VI). The roman numeral notations for oxidation state identify that the plutonium is the central atom of an oxo-complex in water. Thus, the species in water, which corresponds to Pu(VI) is PuO_2^{+2}, and for Pu(V) is PuO_2^{+1}. The chemistry of plutonium is quite complex. A solution of plutonium initially of one oxidation state will undergo several different disproportionation and oxidation reduction reactions until all four of the above oxidation states are present. This peculiar chemistry for plutonium requires sample storage and analytical separations to have significant types of chemical additives to ensure that plutonium is maintained in the proper oxidation state for analysis and separation. Plutonium also has the ability to form long polymeric type chains, where the molecular weight of the chain can reach several thousand daltons. This occurs when storage of solutions is allowed for long time periods (greater than six months). These chains are not easily solubilized nor broken down, thus the analytical result for plutonium in these samples will be biased low.

The ability to exist in multiple oxidation states makes separation schemes for plutonium somewhat interesting. Plutonium can react with inorganic ions like nitrates, chlorides and fluorides to form anionic complexes in the +3 or +4 oxidation state. However, these complexes are not formed in the (V) or (VI) oxidation state due to steric interference from the oxygen atoms. The differences in these chemistries can be advantageously used to separate the different oxidation states of plutonium (i.e., chemical speciation) in an individual sample, or it can be used to separate all plutonium isotopes from other transuranics that behave as cations (e.g., Th, Am, Cm). In a specific application of this behavior, Kim et al. (2000) used a TRU® resin to concentrate all the cationic transuranic ions. The Pu was present as the +4 ion due to oxidation with acidic nitrite. The americium was eluted in dilute HCl, and then the plutonium was reduced back to the +3 oxidation state in HCl, causing the anionic chloro- complex to form, releasing the plutonium from the column.

Separation techniques for plutonium also include solvent extraction and precipitation methods. In every case, the separation of this element requires several layers of analytical techniques. First to remove the bulk of the elements in the first row transition series, then to separate out each of the transuranics individually. The final step in plutonium separation prior to analytical determination is either precipitation or electroplating. In the former, the Pu^{+4} will be separated via coprecipitation with neodymium, cerium, or lanthanum fluoride. In the latter, the plutonium will be plated onto a platinum, stainless steel, or nickel disc in an infinitely thin film.

The analytical separation of plutonium from other transuranics is not the final hurdle in plutonium analysis. Five different isotopes of plutonium, 238, 239, 240, 241, and 242 all may be found in environmental samples. Plutonium-241 is easily distinguishable because it is the only beta emitter; the rest are alpha emitters. Isotopes 238 and 242 emit distinctly different alpha particle energies from 239 and 240, and each other and are also readily determined via alpha spectrometry. However, ^{239}Pu has alpha particles at 5.156 and 5.144 MeV and ^{240}Pu has alpha particles at 5.168 and 5.124 MeV. These alpha particle energies are not significantly different, and cannot be resolved via alpha spectrometric techniques. The half-lives of these two isotopes are sufficiently long so that neither significantly decays during the sampling and analysis time frame. Thus it is common to report the results for these two isotopes together, as a single value.

If the analytical value for each of these isotopes is necessary, then techniques such as ICP-MS, TIMS, or AMS are required. These techniques will be able to separate these two isotopes based on their mass so that individual values may be obtained, however the current cost of such analyses are very high compared to conventional analytical methodologies.

5.13 Radium

Radium has no stable isotopes. It is a member of the uranium and thorium natural decay chains. The isotopes that are normally encountered in environmental samples are ^{223}Ra ($t_{½} \approx 11.4$ d), ^{226}Ra (from ^{235}U and ^{238}U decay), and ^{224}Ra ($t_{½} \approx 3.66$ d) and ^{228}Ra (from ^{232}Th decay). Radium-226 ($t_{½} \approx 1.60 \times 10^3$ y) is the most abundant isotopic form, decaying by emission of an alpha particle to produce ^{222}Rn. The next most abundant isotope is ^{228}Ra ($t_{½} \approx 5.76$ y), which decays by β^- emission. Radium is most closely associated with uranium and thorium ore deposits. Interaction with the soil and ground water will cause some of the radium to become separated from the parent ore due to differences in chemical solubility. When this occurs, and the radium is found “free” in soil or water, it is said to be “unsupported.”

Historically, radium has been extracted from ores through barium sulfate precipitation. The radium isotopes have been used to produce luminous paints and for radiation therapy. While neither of these have current application, there are many sources that were made in the early Twentieth Century that remain uncontrolled. Radium sources are used for measuring metal or material thicknesses, as a source of actinium and polonium (used to produce anti-static devices), and as a neutron source (when mixed with beryllium).

Radium is in the same group in the Periodic Table as barium and calcium. Its chemical properties are very closely related to these two elements. Its only oxidation state is +2. Radium salts that are soluble are chloride, bromide nitrate, and hydroxide. Carbonate, phosphate, and fluoride are sparingly soluble, while sulfate is the most insoluble. Procedures for the separation of radium almost universally rely on barium as the means to coprecipitate radium as the sulfate.

Radium is not soluble in organic solvents or solvents combined with many chelating agents. This provides a convenient means of separation of radium from many other radionuclides, especially the transuranics. It forms weak complexes with EDTA and most inorganic complexing agents. However, it is very strongly complexed by diethylenetriamine pentaacetic acid (DTPA), as a -3 anion.

In dilute acid solution, radium is present as the divalent cation. Because many other radionuclides form anionic complexes in dilute HCl, radium is easily separated from many other radionuclides using a cation exchange resin. Additionally, newly developed ion-exchange filters that contain radium-selective chelants have been used successfully to concentrate radium directly from environmental waters.

Ironically, the two major isotopes of radium may not be measured directly when trying to assess low level concentrations. The radium is concentrated from a large volume of water, and its progeny ^{222}Rn is allowed to in-grow for up to 21 days. The radon gas is sparged into a closed container, allowed to equilibrate with its progeny (total of about 10 hours), and then counted with a special device known as a “Lucas Cell” (alpha scintillation cell) using a photomultiplier tube. This technique is known as “radon emanation.” It is very effective for ^{226}Ra analysis because of the physical separation of its first progeny, ^{222}Rn (a noble gas), by expulsion into the evacuated Lucas Cell. The Lucas Cell is calibrated with a known ^{226}Ra source using radon emanation. The calibration is therefore specific for ^{222}Rn and all its progeny, which come into secular equilibrium with ^{222}Rn (see Section B.1.6, “Radioactive Equilibrium,” on page 76).

Radium-228 is a very low-energy beta emitter (0.039 MeV) and does not lend itself to low MDCs using gas proportional counting. However the first progeny of ^{228}Ra is ^{228}Ac ($t_{1/2} \approx 6.2$ h), which achieves equilibrium with the radium in about 36 hours. It can be measured by either gas proportional counting or by gamma spectrometry.

5.14 Strontium

Strontium has four stable isotopes. Its principal radioisotopes are ^{89}Sr and ^{90}Sr (both a result of fission of uranium or plutonium), ^{85}Sr (used principally as a radiotracer), and ^{82}Sr. Radiostrontium sources are used as depth measurement devices, calibration sources, environmental and biological tracers, and in the treatment of some cancers.

Strontium is a member of Group II of the Periodic Table and is chemically related to both barium and radium. It has only one oxidation state, +2, thus making its chemistry very straightforward. The soluble salts of strontium are chloride, fluoride, acetate, nitrate, chlorate, and permanganate. The hydroxide and the carbonate are slightly soluble. Strontium oxalate and sulfate are fairly insoluble. Both have been used to separate strontium gravimetrically. The nitrate can be made insoluble in fuming nitric acid, and this technique has been used as a means of chemical separation.

Strontium does not form strong complexes. The most significant one is with EDTA, which is used in many separation schemes for isolation of strontium from other radionuclides. Because of its poor ability to complex, it is present as a cation in most solutions. This can be used advantageously to separate it from other metals that can form anionic complexes. Thus, complexing transition metals like cobalt, nickel, or iron with chlorides, and using an anion-exchange resin, will bind the anionic complexes to the resin allowing strontium be removed. Alternatively, the complexed solution may be passed through a cation resin, which will retain the strontium, while the other complexed radionuclides pass through the column.

The two principal long-lived isotopes of strontium produced from fission are ^{89}Sr ($t_{½} \approx 50.5$ d) and ^{90}Sr ($t_{½} \approx 28.8$ y). Both are beta emitters, and because they are the same element, they cannot be separated chemically. Their β-particle energies are not sufficiently different to be easily distinguished using gas proportional or liquid scintillation counting techniques.

Several techniques have been devised to deal with this problem. A popular indirect method can be used to analyze both strontium radionuclides. It initially counts the separated strontium isotopes. The separated strontium is allowed to build up ^{90}Y ($t_{½} \approx 64$ h) over a defined period of up to about two weeks. The ^{90}Y is then separated chemically from the strontium radionuclides, and analyzed. Due to the laws of radioactive equilibrium (see Appendix B), the amount of ^{90}Sr that produced the ^{90}Y can be calculated. This can be subtracted from the initial total strontium activity to yield an activity of ^{89}Sr. This limits the MDCs that can be achieved and also increases the analytical uncertainty close to the MDC.

Samples of soil or water from areas not directly impacted by an operating nuclear facility or recent weapons testing are not likely to contain ^{89}Sr, due to its short half-life. However, in effluents from nuclear facilities and some wastes, both radionuclides will be present. (It should be noted that ^{140}Ba may also be present in these types of samples.) Because the chemistry of barium and strontium are so similar, the analytical separations process should specifically eliminate barium. This is usually performed through a $BaCrO_4$ precipitation (the strontium salt is soluble).

Yield for strontium analysis is determined either gravimetrically by using stable strontium carrier or by using a ^{85}Sr radiotracer. When a strontium carrier is employed, the carbonate or oxalate is precipitated, dried, and weighed. The amount also may be determined by atomic absorption spectrometry. Using ^{85}Sr radiotracer, the decay is by electron capture and gamma emission, thus allowing an independent method (gamma spectrometry) of determining its yield without interfering with the beta analysis.

5.15 Sulfur

Sulfur is similar to phosphorus and carbon in that it forms many chemically stable organic compounds through covalent bonding. In environmental water samples, sulfur mainly exists as sulfate (SO_4^{-2}). Other inorganic forms of sulfur are sulfide (S^{-2}), thiosulfate ($S_2O_3^{-2}$), sulfite (SO_3^{-2}), and sulfur dioxide (SO_2). Sulfur has oxidation states -2,+2, +4, and (VI), and they can be present in both organic and inorganic compounds.

Sulfur has one long-lived radioisotope (^{35}S, $t_{1/2} \approx 87$ d), which when incorporated into organic materials, is a radiotracer for the specific characteristics of the organic material. This radionuclide is a beta-only emitter ($E_{\beta max} = 0.167$ MeV) and can be detected using either liquid scintillation or GPC.

Environmental samples that contain sulfur are subject to attack by microorganisms, which can change the oxidation state of the sulfur. *Desulfovibrio desulfuricans* is a sulfate-reducing bacterium, ubiquitous in the soil sample, which can change oxidized sulfur species into hydrogen sulfide. Thus, it is important to know the condition of the sampling so that loss of this isotope as a result of this bacteria can be addressed.

As with phosphorus, if sulfur may be present as part of an organic compound, then sampling and analytical protocols need to address that particular compound. One means of separation from other materials is that sulfur can be oxidized to sulfate and easily separated by gravimetric analysis. Acid digestion or sample combustion with stable sulfate as a carrier can be successfully employed for yield determination of the sample digestion process.

5.16 Technetium

Technetium is an oddity in the middle of the Periodic Table; it has no stable isotopes. Any primordial technetium has decayed away because its longest-lived isotope, ^{98}Tc, has a half-life of only 4.2×10^6 years. The most significant isotope produced as a result of nuclear fission, ^{99}Tc, has a half-life of 2.1×10^5 years. It decays by emission of a beta particle ($E_{\beta max} = 0.29$ MeV). In the environment, very small quantities of this isotope can be ascribed to the natural fission process of uranium ores.

Technetium-99 is the most significant technetium isotope present in wastes from nuclear power plants, especially in spent fuel. Medical wastes are an additional source of ^{99}Tc, because ^{99m}Tc (the "m" is for "metastable") is used as a radio-imaging isotope for oncological assessments. The isomeric isotope ^{99m}Tc has a half-life of only six hours, and decays directly to the ground state, ^{99}Tc through gamma emission.

The chemistry of technetium is very similar to that of rhenium. The most common oxidation states of technetium are (+4) and (VII). In an oxidative environment, technetium will be present as the pertechnetate ion, TcO^-_4, which has significant mobility in ground water (i.e., not well retained by soils). In reducing environments, technetium will form partially soluble TcO_2.

Technetium forms complexes with organic and inorganic ligands under many different conditions and can be easily separated from other radionuclides using ion chromatography. Radiochemical analysis for ^{99}Tc can be performed by GPC, using the gamma emitter ^{99m}Tc ($t_{1/2} \approx 6$ h) to monitor yield. In ICP-MS and some gravimetric analyses, rhenium is used as a yield monitor for technetium.

5.17 Thorium

Thorium is the second member of the actinide series. It has as its principal isotope ^{232}Th, which has a half-life of 1.4 × 10^{10} years. Thorium is naturally occurring and is a normal radioactive constituent of cement and concrete. Thorium has five additional naturally occurring radioisotopes (227, 228, 230, 231, and 234, with half-lives of 18.7 d, 1.91 y, 7.54 × 10^4 y, 1.06 d, and 24.1 d, respectively) that result from the uranium and thorium decay chains.

The presence of thorium is often not discovered directly, but through the radioactive emissions of its progeny radium, actinium, polonium, bismuth, and lead. Thorium is a refractory material with a very high melting point.

The chemistry of thorium in solution is relatively simple because it is difficult to reduce to the metal, and it only has one oxidation state, +4. Although thorium is more abundant in the Earth's crust than uranium by an order of magnitude, it is much more insoluble than uranium and is less commonly encountered in surface and ground water. The soluble compounds of thorium include the nitrate, sulfate, chloride and perchlorate. Most other thorium compounds (particularly hydroxide, fluoride, and phosphate) are insoluble in water. Therefore, the pH of the environment in which the thorium radionuclides exist will determine its mobility.

Thorium is most likely present as a hydrated cation below a pH of 3.0. Above pH 3.0 the thorium most likely exists as a colloid. This property makes it easily amenable to separation from other trace constituents by flocculation (like using a ferric or aluminum hydroxide precipitate). Thus it is important to maintain a low pH and avoid precipitates (even at the low pH) so that thorium will not be dissipated into different phases as a result of this colloidal behavior.

Soil samples analyzed for thorium should be completely dissolved. Acid leaching of the soil may not be sufficient to solubilize all the thorium. Fusion using sodium carbonate, potassium fluoride, and potassium bisulfate generally will provide the best means of bringing the thorium into the melt and successfully solubilizing it in subsequent steps.

Many inorganic and organic thorium compounds and complexes are soluble in organic solvents. This is due to the large size of the thorium ion, which results in a relatively low charge density of the ion and its complexes and compounds. This property forms the basis of several different separation schemes for thorium. Thorium also forms several different types of anionic and cationic complexes in aqueous solutions that can be used to successfully separate thorium from other cations. One such method is the use of concentrated nitric acid to separate thorium from other actinides and its progeny using an anion exchange resin. The hexanitrato-thorate complex is strongly bound to the anion resin while other cations pass through.

Analyses of ^{227}Th, ^{228}Th, ^{230}Th, and ^{232}Th are usually performed by alpha spectrometry or GPC. Thorium-229 has been used as a yield monitor for alpha spectrometric analysis of these radionuclides because it is not commonly encountered.

Thorium-231 ($t_{½}$ ≈ 1.1 d) and ^{234}Th ($t_{½}$ ≈ 24 d) are both beta emitters and first progeny of ^{235}U and ^{238}U, respectively. Their short half-lives make them good markers for the relative amounts of these two uranium isotopes. Thorium-234 is also a gamma emitter. However, its gamma rays are in the low energy end of the spectrum (<100 keV) and are generally obscured by background radiation if measurable quantities of other gamma emitters are present.

5.18 Uranium

Uranium is the last of the naturally occurring elements in the Periodic Table. Although it has no stable isotopes, the long half-life of ^{238}U ($t_{½} \approx 4.47 \times 10^9$ y) and ^{235}U ($t_{½} \approx 7.0 \times 10^8$ y) makes their presence in the environment possible. Long before uranium was associated with radioactivity, it was known as a ceramic glaze. The brilliant orange color that its oxide imparts to pottery made it popular through the 1930s. Although identified on the chart of the nuclides as a naturally occurring isotope, ^{234}U is present as a result of being the third progeny of the ^{238}U decay chain. Its natural abundance of 0.0055 is due solely to the ^{238}U decay chain.

Uranium has several different oxidation states that exist in solution chemistry and several may be stable in the environment. The most common oxidation state is (VI) as the uranyl ion, UO_2^{2+}. This oxo-complex of uranium has a significant effect on its solution chemistry. Although the uranium has an oxidation number of (VI), the ion in solution has a +2 charge and may behave as an anion due to the effect of the bulky, negative oxygen atoms attached to the central uranium ion. The +3, +4, and (V) oxidation states also can be stable in solution. The U(V) ion is present as the UO_2^{+1} ion, and may disproportionate to yield U^{+4} and U(VI), if not appropriately stabilized.

Uranium has special significance because it is part of the uranium fuel cycle used for nuclear power reactors and also used for nuclear weapons. The enrichment process (by ultracentrifugation or gas diffusion) leaves a material behind that is depleted in the fissionable isotope, ^{235}U. This leftover material is designated “depleted uranium” (DU). DU has a use in conventional weapons as antitank ordnance due to its high density. It also may be used as ballast on commercial airliners. In both instances, these are still radioactive materials and should be handled appropriately. Although of little value for direct fission, DU can be used as a blanketing material in a breeder reactor to absorb neutrons and form ^{239}Pu, which is fissile.

Uranium is soluble in water in part due to its ability to complex with the carbonate ion. Uranium forms a myriad of carbonate complexes from pH 1 to 14. Solubility of uranium compounds is directly dependent upon the oxidation state of the uranium. With the exception of fluoride, uranium (+3 and +4) halide compounds are water soluble. The U(VI) compounds follow their own rule of solubility, and the sulfate, bicarbonate, carbonate, chromate tungstate, and nitrate are all soluble.

The solution chemistry of uranium is probably more extensive than that of any other radionuclide. It has many different organic complexes that it can form and be extracted into various solvents. It complexes with many inorganic and organic ions to form cationic and anionic complexes. Two of the most significant solution characteristics of uranium will be described here. Uranium as the uranyl ion (VI), will not precipitate or coprecipitate in fluoride media. The oxygen atoms attached to the uranium inhibit the precipitation of uranium. However if the uranium is reduced using $TiCl_3$, to U^{+4}, the uranium will easily coprecipitate with either neodymium or lanthanum fluoride. The other anomalous behavior of uranium is related to ion exchange capability. The U(VI) ion is less strongly bound to cation resin than the +4 oxidation state, again due to the bulky, negative field established by the two oxygen atoms on the U(VI) ion.

U(VI) will form strong anionic complexes with halides, and these have been used as separation techniques from other transuranics using an anion resin material.

All of the naturally occurring uranium isotopes are alpha emitters. Analysis for uranium isotopes may use ^{232}U ($t_{½} \approx 68.9$ y) as a radiotracer, because it is not part of any decay series. Uranium-232 is a long-lived alpha emitter, whose alpha particles can be easily distinguished from the other uranium isotopes. Uranium may also be analyzed by its ability to phosphoresce chemically. This is a very unique property of uranium based solely on its chemical structure and having nothing to do with its being radioactive. None of the other transuranic elements possess this particular capability thus distinguishing uranium by this property. This analytical methodology is used for concentrations of uranium in the part-per-million range and above. It should be noted that the presence of uranium in environmental samples means that all of its progeny will be present to a varying extent based on solubility.

6 Reference Materials

6.1 Citations

American Society for Testing and Materials (ASTM) C1345, *Standard Test Method for Analysis of Total and Isotopic Uranium and Thorium in Soil by Inductively Coupled Plasma-Mass Spectrometry*, 2001 West Conshohocken, PA.

American Society for Testing and Materials (ASTM) D5673, *Standard Test Method for Elements in Water by Inductively Coupled Plasma-Mass Spectrometry*, 2003 West Conshohocken, PA.

Benitez-Nelson, C.R. and K.O. Buesseler. 1998. "P-32 and P-33 Activities in Rainwater and Seawater," *Anal. Chem*. 70, p. 64.

U.S. Central Intelligence Agency (CIA). 2003. Terrorist CBRN: Materials and Threats (U). CTC 2003-40058. 6 pp.

Cecil, L.D., L.F. Hall, and J.R. Green. 2003. "Reevaluation of Background Iodine-129 Concentrations in Water from the Snake River Plain Aquifer, Idaho." U.S. Geological Survey Water-Resources Investigations Report 03-4106, prepared in cooperation with the U.S. Department of Energy, DOE/ID-22186. Available at: http://pubs.usgs.gov/wri/wri034106/.

Chiarappa-Zucca, M.L., K.H. Dingley, M.L. Roberts, C.A. Velsko, and A.H. Love. 2002. "Sample Preparation for Quantitation of Tritium by Accelerator Mass Spectrometry,"*Anal. Chem.*, 74, p. 6285.

U.S. Department of Energy (DOE) 1997a. *Linking Legacies: Connecting the Cold War Nuclear Weapons Production Processes To Their Environmental Consequences* (DOE/EM-0319). Office of Environmental Management, Washington, DC. Available at: legacystory.apps.em.doe.gov/index.asp.

U.S. Department of Energy (DOE) 1997b. *EML Procedures Manual*, Chieco, N.A., Bogen, DC., and Knutson, E.O., Eds., HASL-300, 28th Edition, DOE Environmental Measurements Laboratory, New York. Available at: http://www.eml.st.dhs.gov/publications/procman/.

U.S. Environmental Protection Agency (EPA). 1994. *Methods for the Determination of Inorganic Substances in Environmental Samples, Supplement 1*. EPA Method 200.8 (Rev 5.4). EPA/600/R-93/100. Publication PB95-125472 available to order from National Technical Information Service, 5285 Port Royal Road, Springfield, VA 22161, www.ntis.gov/search/product.asp?ABBR=PB95125472&starDB=GRAHIST.

U.S. Environmental Protection Agency (EPA). 1997. "Establishment of Cleanup Levels for CERCLA Sites with Radioactive Contamination." Washington, DC: Office of Emergency and Remedial Response and Office of Radiation and Indoor Air. OSWER Directive 9200.4-18, August 22. Available at www.epa.gov/superfund/resources/radiation/pdf/radguide.pdf.

U.S. Environmental Protection Agency (EPA). 1999. *Understanding Variation in Partition Coefficient, K_d, Values*, Volumes I and II. Washington, DC: Office of Air and Radiation, EPA 402-R-99-004A&B. Available at: www.epa.gov/radiation/cleanup/partition.htm.

U.S. Environmental Protection Agency (EPA). 2000. *Soil Screening Guidance for Radionuclides: User's Guide*. Washington, DC: Office of Radiation and Indoor Air and Office of Solid Waste and Emergency Response, EPA/540-R-00-007. OSWER Directive 9355.4-16A. Available at: www.epa.gov/superfund/resources/radiation/radssg.htm#user.

U.S. Environmental Protection Agency (EPA). 2002. *Implementation Guidance for Radionuclides*. Washington, DC: Office of Ground Water and Drinking Water (4606 M), EPA 816-F-00-002. Available at: www.epa.gov/safewater/rads/final_rads_implementation_guidance.pdf

Demange, D., M. Grivet, H. Pialot, and A. Chambaudet. 2002. "Indirect Tritium Determination by an Original ^{3}He Ingrowth Method Using a Standard Helium Leak Detector Mass Spectrometer," *Anal. Chem.*, 74, p. 3183.

U.S. Food and Drug Administration (FDA). 2004. *Supporting Document for Guidance Levels for Radionuclides in Domestic and Imported Foods* [Docket No. 2003D-0558]. Center for Food Safety and Applied Nutrition, Office of Plant and Dairy Foods and Beverages. Available at www.cfsan.fda.gov/~dms/nucleve2.html.

Friedlander, G., Kennedy, J.W., Macias, E.S., and Miller, J.M. 1981. *Nuclear and Radiochemistry*, John Wiley and Sons, New York.

Health Physics Society. Online fact sheet on naturally occurring radioactive materials (NORM), available at: hps.org/publicinformation/ate/q1009.html.

Interagency Working Group on Radiological Dispersal Devices (IWGRDD). 2003. *Radiological Dispersal Devices: An Initial Study to Identify Radioactive Materials of Greatest Concern and Approached to Their Tracking, Tagging, and Disposition*. Report to the Nuclear Regulatory Commission and the Secretary of Energy, May.

Kim, G., W.C. Burnett, and E.P. Horwitz. 2000. "Efficient Preconcentration and Separation of Actinide Elements from Large Soil and Sediment Samples," *Anal. Chem*., 72, p. 4882.

Lapp, R.E. and H.L. Andrews. 1964. *Nuclear Radiation Physics*, 3rd Edition. Englewood Cliffs: Prentice Hall.

MARLAP. 2004. *Multi-Agency Radiological Laboratory Analytical Protocols Manual*. Volumes 1 – 3. Washington, DC: EPA 402-B-04-001A-C, NUREG 1576, NTIS PB2004-105421. July. Available at www.epa.gov/radiation/marlap/manual.htm.

MARSSIM. 2000. *Multi-Agency Radiation Survey and Site Investigation Manual, Revision 1*. NUREG 1575 Rev 1, EPA 402-R-97-016 Rev1, DOE/EH-0624 Rev1. August. Available at: www.epa.gov/radiation/marssim/index.html.

U.S. Nuclear Regulatory Commission (NRC). 1984. *Long-Lived Activation Products in Reactor Materials*. NUREG/CR-3474. NRC, Washington, DC.

U.S. Nuclear Regulatory Commission (NRC). 1997. *Minimum Detectable Concentrations with Typical Radiation Survey Instruments for Various Contaminants and Field Conditions.*. NUREG/CR-1507. NRC, Washington, DC.

U.S. Nuclear Regulatory Commission (NRC). 2004. *Fact Sheet on Decommissioning Nuclear Power Plants*. NRC, Washington, DC. Available at www.nrc.gov/reading-rm/doc-collections/fact-sheets/decommissioning.html.

Office of Technology Assessments (OTA). 1991. *Complex Cleanup: The Environmental Legacy of Nuclear Weapons Production*. Congress of the United States, Office of Technology Assessments, OTA-O-484, NTIS #PB91-143743, February.

Ognibene, Ted J., Graham Bench, John S. Vogel, Graham F. Peaslee, and Steve Murov. 2003. "A High Throughput Method for the Conversion of CO_2 Obtained from Biochemical Samples to Graphite in Septa-sealed Vials for Quantification of ^{14}C Quantification via Accelerator Mass Spectrometry," *J. Anal. Chem*. 75, pp. 2192-2196.

Rollin, Stefan, and Ulla-Britt Eklund. 2000. "Determination of U(IV) and U(VI) by Ion Chromatography-Inductively Coupled Plasma Mass Spectrometry and Its Application to Kinetic Studies," *J. Chromatogr. A*, 884, pp. 131-141.

Schultz, M.K., W. Burnett, K.G.W. Inn, and G. Smith. 1998. "Geochemical Partitioning of Actinides Using Sequential Chemical Extractions: Comparison to Stable Elements," *J. Radioanal. Nucl. Chem.*, 234, p. 251.

Shebell, P. 2003. "An In Situ Gamma-ray Spectrometry Intercomparison," *Health Physics*, 85(6), pp. 662 - 677.

Truscott, James B., Phil Jones, Ben E. Fairman, and El Hywel Evans. 2001. "Determination of Actinides in Environmental and Biological Samples Using High Performance Chelation Ion

Chromatography Coupled to Sector-Field Inductively Coupled Plasma Mass Spectrometry,"*J. Chromatogr. A,* 928, pp. 91-98.

6.2 Other Sources

Adolff, J.-P. and Guillaumont, R. 1993. *Fundamentals of Radiochemistry*, CRC Press, Boca Raton, Florida.

American Public Health Association (APHA). 1998. *Standard Methods for the Examination of Water and Waste Water, 20th Edition*. Washington, DC. Available at: www.standardmethods.org.

Choppin, G., Rydberg, J., Liljenzin, J.O. 1995. *Radiochemistry and Nuclear Chemistry*, Butterworth-Heinemann, Oxford.

Coomber, D.I., Ed. 1975. *Radiochemical Methods in Analysis*, Plenum Press, New York.

Eisenbud, Merril, and Thomas Gesell. 1997. *Environmental Radioactivity from Natural, Industrial, and Military Sources*. Fourth Edition. San Diego: Academic Press. 656 pp.

U.S. Environmental Protection Agency (EPA). 1980. *Upgrading Environmental Radiation Data, Health Physics Society Committee Report HPSR-1*, EPA, 520/1-80-012, EPA, Office of Radiation Programs, Washington, DC.

Federal Radiological Monitoring and Assessment Center (FRMAC). 2004. *FRMAC Laboratory Analysis Manual*. Las Vegas, NV: U.S. Department of Energy, National Nuclear Security Administration, Nevada Support Facility (DOE/NV/11718–852). Available at: www.nv.doe.gov/library/publications/frmac/DOENV11718_852.pdf.

Gilmore, G. and J.D. Hemingway. 1995. *Practical Gamma-Ray Spectrometry*, John Wiley, Chichester.

Gy, Pierre M. 1992. *Sampling of Heterogeneous and Dynamic Material Systems: Theories of Heterogeneity, Sampling, and Homogenizing*. Amsterdam: Elsevier.

Horrocks, D.L. 1970. *Applications of Liquid Scintillation Counting*, Academic Press.

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

International Organization for Standardization (ISO). 1993b. *Statistics – Vocabulary and Symbols – Part 1: Probability and General Statistical Terms*. ISO 3534-1. ISO, Geneva, Switzerland.

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

International Organization for Standardization (ISO). 1997. *Capability of Detection – Part 1: Terms and Definitions*. ISO 11843-1. ISO, Geneva, Switzerland.

International Union of Pure and Applied Chemistry (IUPAC). 1995. Nomenclature in Evaluation of Analytical Methods Including Detection and Quantification Capabilities. *Pure and Applied Chemistry* 67:10, pp. 1699–1723.

Knoll, G. F. 1989. *Radiation Detection and Measurement*, 2nd Edition. New York: John Wiley & Sons.

McDowell, C.A. 1963. *Mass Spectrometry*. (Editor) New York: McGraw-Hill Book Co.

Mann, W.B., A. Rytz, and A. Spernol. 1991. *Radioactivity Measurements, Principles and Practice*. New York: Pergamon Press (previously published in *Applied Radiation and Isotopes*, 38:8, 1988, pp. 717-937).

U.S. Nuclear Regulatory Commission (NRC). 1978. *Technology, Safety and Costs of Decommissioning a Reference Pressurized Water Reactor Power Station*.. NUREG/CR-0130. NRC, Washington, DC.

U.S. Nuclear Regulatory Commission (NRC). 1984. *Lower Limit of Detection: Definition and Elaboration of a Proposed Position for Radiological Effluent and Environmental Measurements*. NUREG/CR-4007. NRC, Washington, DC.

Parrington, J.R., Knox, H.D., Breneman, S.L., Feiner, F., and Baum, E.M. 1996. *Nuclides and Isotopes: Chart of the Nuclides*. 15th Edition. Lockheed Martin and General Electric.

Ross, R.R., J.R. Noyce, and M.M. Lardy. 1993. "Inductively Coupled Plasma-Mass Spectrometry: An Emerging Method for Analysis of Long-Lived Radionuclides," *Radioactivity and Radiochemistry*, 4:1, pp. 24-37.

Shleien, Bernard, ed. 1992. *The Health Physics and Radiological Health Handbook*. Silver Spring, MD: Scinta Inc.

Wahl, A.C. and Bonner, N.A. 1951, Second Printing: May, 1958. *Radioactivity Applied to Chemistry*, John Wiley and Sons, New York.

Appendix A: Glossary

(Note: terms in italics within definitions contain their own entries)

***activity (A), radioactive*:** (1) The rate of nuclear transformations of a radioactive substance, i.e., the number of *radioactive* atoms undergoing nuclear transformation (nuclear decay) per unit time; (2) The number of nuclear decays occurring in a given quantity of material in a small time interval, divided by the time interval: $A = -dN/dt$.

***alpha particle* (α):** Essentially a helium nucleus, comprised of two protons and two neutrons ($Z = 2$, $A = 4$). An α particle is the heaviest particle emitted during *radioactive decay*.

***analytical data requirements*:** Measurement performance criteria used to select and decide how the laboratory analyses will be conducted and used for the initial, ongoing, and final evaluation of the laboratory's performance and the laboratory data. *Analytical data requirements* are often described in terms of sensitivity (method detection capability), completeness, precision, and accuracy or bias. In a performance-based approach, the project-specific *analytical data requirements* serve as measurement performance criteria and decisions on how the laboratory analyses will be conducted, e.g., method selection, etc.

***analytical method*:** A major component of an analytical protocol that normally includes written procedures for sample digestion, chemical separation (if required), and counting (analyte quantification through *radioactive* decay emission or atom counting measurement techniques.

***analytical protocol*:** A compilation of specific procedures/methods that are performed in succession for a particular analytical process. With a performance-based approach, there may be a number of appropriate analytical protocols for a particular analytical process. The *analytical protocol* is generally more inclusive of the activities that make up the analytical process than is the analytical method. See *analytical method*.

***analytical protocol specification* (APS):** The output of a directed planning process that contains the project's analytical data needs and requirements in an organized, concise form. The level of specificity in the APS should be limited to those requirements that are considered essential to meeting the project's analytical data requirements to allow the laboratory the flexibility of selecting the protocols or methods that meet the analytical requirements.

***atomic mass* (A):** The sum of an atom's protons (Z) and neutrons (N); also called "atomic weight." Isotopes of a given element all have the same number of protons but different numbers of neutrons, so they have different masses (see *atomic number*).

***atomic number* (Z):** The number of protons in an atom's nucleus. The atomic number defines an element's chemical properties, and hence its place in the Periodic Table.

***becquerel* (Bq):** The SI unit of radioactivity, defined as one disintegration (decay) per second. The more common unit is the picocurie (pCi) or 10^{-12} Ci, which equals 2.22 disintegrations per minute (dpm), or 0.037 Bq. See *curie*.

beta particle**:** Beta particles (β^-) and ***positrons*** (β^+) are essentially electrons, but they originate in the nucleus of an atom. A ***conversion electron*** (e^-) is generated from the interaction of a *gamma ray* with an orbital electron. All of these particles have the same mass and charge. *Conversion electrons* are *monoenergetic*, having the energy of the *gamma ray* minus the energy needed to remove the electron from orbit. *Beta particles* and *positrons* always have an energy distribution from zero to a maximum.

branching decay**:** This occurs when a *radionuclide* can decay by more than one mode. Examples of this would be ^{235}U decaying by alpha emission or by spontaneous fission, or ^{214}Bi decaying by β^- or α emission. Generally, for any radionuclide, one possible decay mode predominates by orders of magnitude. The half-life denoted is the aggregate half-life of all the decay modes, proportional to their percent abundance. However, each branching decay has its own half-life.

branching fraction**:** The fraction of particles or photons with a specific energy that result from the decay of a particular *radionuclide*. For example, the branching fractions for the ^{134}Cs γ rays at 795 and 605 keV are 0.854 and 0.976, respectively (for every 1,000 decay events, 854 and 976 of these γ rays, respectively would be emitted). Also referred to as "branching ratio," "emission probability," and "particle yield."

bremsstrahlung radiation**:** When an electron passes through matter, it can undergo a very large acceleration (deceleration). The resulting loss by the electron of radiant energy (photons) is called *bremsstrahlung* (from the German "bremsen," to brake, and "Strahlung") radiation.

carrier**:** A stable isotope of an element (usually the analyte) added to increase the total amount of that element so that a measurable mass of the element is present.

carrier-free radiotracer**:** (1) A *radioactive* isotope tracer that is essentially free from stable (non-radioactive) isotopes of the element in question. (2) Addition of a specific, nonradioactive isotope of an element to change the measured isotopic abundance of the element in the sample. Such materials are usually designated as nonisotopic material or marked with the symbol "c.f." (see *carrier*, *radiotracer*).

Cerenkov radiation**:** Cerenkov radiation is emitted in the ultraviolet spectrum when a fast charged particle traverses a dielectric medium (like water) at a velocity exceeding the velocity of light in that medium. It is analogous to the "sonic boom" generated by a craft exceeding the speed of sound.

check source**:** A sealed source used to verify the operabilitly of an installed radiation detector. The source is shielded from the detector except during brief intervals when it is inserted in front of the active detector surface. The response that the detector yields must be above a certain number of counts for the detector to be considered operable.

chelate**:** A class of metal-organic or metal-inorganic compounds in which the metal atom or ion is held by a pair of *ligand* atoms in a single molecule.

constant weight**:** A process by which a sample is heated in an oven at about 105 °C for at least one hour, cooled in a desiccator, then weighed. This process is performed at least twice so that two successive mass determinations agree to within a range determined by the analytical protocols for the project.

conversion electron**:** See *beta particle*.

counting efficiency**:** the ratio of the events detected (and registered) by a radiation detection system to the number of particles or photons emitted from a *radioactive* source. The counting efficiency may be a function of many) variables, such as radiation energy, source composition, and source or detector geometry.

count time**:** The time interval for the counting of a sample or source by a radiation detector (also referred to as the "live" time or analysis time).

critical value**:** In the context of analyte detection, the minimum measured value (e.g., of the instrument signal or the analyte concentration) required to give confidence (to a given probability) that a positive (different than background) amount of analyte is present in the material analyzed. The critical value is sometimes called the *critical level* or *decision level*.

cross-contamination**:** Cross-contamination occurs when *radioactive* material in one sample is inadvertently transferred to an uncontaminated sample, which can result from using contaminated sampling equipment and chemicals, and improperly cleaned glassware, crucibles, grinders, etc. Cross-contamination may also occur from spills, as well as airborne dusts of contaminated materials created during grinding.

crosstalk: A phenomenon in gas proportional counting or liquid scintillation counting when an emission of an *alpha* particle is recorded as a *beta* particle count or vice versa. This is due to the ionization affects of the particles at different energies.

***curie* (Ci):** The common unit of radioactivity. Originally defined as the radioactivity of 1 g of pure radium; since 1953 defined as exactly 3.7×10^{10} disintegrations per second, or 3.7×10^{10} Bq. Because the Ci is such a large value, the more common unit is the picocurie, or 10^{-12} Ci. See *becquerel*.

data package**:** The information the laboratory should produce after processing samples so that data verification, validation, and quality assessment can be done.

***Data Quality Objective* (DQO):** DQOs are qualitative and quantitative statements that clarify the study objectives, define the most appropriate type of data to collect, determine the most appropriate conditions from which to collect the data, and specify tolerable limits on decision error rates. The DQOs should encompass the total uncertainty resulting from all data collection activities, including analytical and sampling activities.

decay**:** The decrease in the number of atoms of any *radioactive* material with the passage of time due to the spontaneous emission from the nuclei of photons or *alpha* or *beta* particles, often accompanied by *gamma* radiation. Eventually, all *radioactive* materials decay to stable elements. See *radioactive, decay chain*.

decay chain**:** A *decay chain* or decay series begins with a parent radioisotope (also called a parent *radionuclide* or parent nuclide). As a result of the *radioactive decay* process, one element is transformed into another. The newly formed element, the decay product or progeny, may itself be *radioactive* and eventually decay to form another nuclide. Moreover, this third decay product may be unstable and in turn decay to form a fourth, fifth, or more generations of other *radioactive* decay products. The final decay product in the series will be a stable element. Elements with extremely long half-lives may be considered stable in most cases. Examples of important naturally occurring *decay chains* include the uranium series, the thorium series, and the actinium series.

decay emissions**:** The emissions of alpha particles, beta particles, or gamma rays from an atomic nucleus, which accompany a nuclear transformation from one chemical atom to another or from a higher nuclear energy state to lower one.

derived concentration guideline level**:** A derived radionuclide-specific activity concentration within a *survey unit* corresponding to the release criterion. DCGLs are derived from activity/dose relationships through various exposure-pathway scenarios.

eluent**:** The mobile phase in chromatography. Also called "eluant." Elution is the removal, by means of a suitable solvent, of one material from another that is insoluble in that solvent, as in chromatography.

error**:** The difference between a measured result and the true or expected value of the analyte being measured. The error of a measurement is primarily a theoretical concept, because its true value is never known. See also *measurement uncertainty*.

extractant**:** An agent used to isolate or extract a substance from a mixture or combination of substances. An ***extractant scintillator*** extracts the *radionuclide* or element from the solution.

gamma ray **(γ):** After alpha or beta emission, the nucleus may still possess excess energy (i.e., they remain unstable). The extra energy is given off in the form of gamma radiation. Gamma rays, like X-rays, are part of the electromagnetic spectrum (beyond ultraviolet wavelengths), and their energies correspond to the difference in the energy levels in the nucleus from which they come. These discrete energies are used to identify the *radionuclides* from which they originated. Gamma rays typically accompany α, β^-, and β^+ emission but originate from the resultant nucleus of the decay process after the particle emission. See *X-rays*.

gray **(Gy):** The SI unit for absorbed radiation dose. One gray is 1 joule of energy absorbed per kilogram of matter, equal to 100 *rad*.

half-life **($t_{½}$):** The time required for one-half of the atoms of a particular *radionuclide* in a sample to disintegrate or undergo nuclear transformation.

ingrowth**:** The occurrence and increase of a progeny *radionuclide* within a sample, initially containing only the parent *radionuclide*, caused by *radioactive* decay of the parent.

ion-exchange chromatography**:** A separation method based on the reversible exchange of ions in a mobile phase with ions bonded to a solid ionic phase. Ions that are bonded less strongly to the solid phase (of opposite charge) are displaced by ions that bond more strongly bonded. Separation of analyte ions depends on the relative strength of bonding to the solid phase. Those less strongly bonded ions are released from the solid phase earlier and *eluted* sooner.

***isobar*:** Nuclides that have the same *atomic mass number* but a different number of protons (Z) and neutrons (N). Isobars have different chemical properties. For example, ^{36}Cl (Z = 17, N = 19) and ^{36}S (Z = 16, N = 20) are isobars because they have the same atomic mass even though they are chemically different. As *radionuclides*, isobars may be related through *radioactive decay* by β^+, β^-, or electron capture. For example, ^{90}Sr (Z = 38, N = 52) decays to ^{90}Y (Z = 39, N = 51) by β^- emission. These two *radionuclides* are isobars.

***isomeric transition*:** The transition, via gamma-ray emission, of a nucleus from a high-energy state to a lower-energy state without accompanying particle emission, e.g., $^{99m}\text{Tc} \rightarrow {}^{99}\text{Tc} + \gamma$.

***isotope*:** *Nuclides* having the same number of protons in their nuclei (same *atomic number*), but differing in the number of neutrons (different mass number). Thus, hydrogen (Z = 1) has one proton. Tritium (^{3}H) is an atom of hydrogen with one proton and two neutrons, with an *atomic mass* of 3. A "radioisotope" is an isotope with *radioactive* properties. See *nuclide* and *radionuclide*.

***laboratory control sample* (LCS):** (Also referred to as a "QC sample.") A standard material of known composition or an artificial sample (created by fortification of a clean material similar in nature to the environmental sample), which is prepared and analyzed in the same manner as the environmental sample. In an ideal situation, the result of an analysis of the *laboratory control sample* should be equivalent to (give 100 percent of) the target analyte concentration or activity known to be present in the fortified sample or standard material.

***ligand*:** Two atoms of a single molecule holding a metal atom or ion in a *chelate*.

***measurement quality objective* (MQO):** The analytical data requirements of the *Data Quality Objectives* that are project- or program-specific. MQOs can be quantitative or qualitative. MQOs serve as measurement performance criteria or objectives of the analytical process. Quantitative MQOs are statements of required analyte detectability or the uncertainty of the analytical protocol at a specified *radionuclide* concentration, such as the action level. Qualitative MQOs are statements of the required specificity of the analytical protocol, e.g., the ability to analyze for the *radionuclide* of concern given the presence of interferences.

***measurement uncertainty*:** Uncertainty of measurement is defined as a parameter, associated with the result of a measurement, that characterizes the dispersion of values that could reasonably be attributed to the measurand. The uncertainty of a measured value is typically expressed as an estimated standard deviation, called a *standard uncertainty*.

***minimum detectable concentration* (MDC):**The MDC is the "true" concentration of analyte required to give a specified high probability that the measured response will be greater than the critical value. The International Standards Organization (ISO) refers to the MDC as the "minimum detectable value of the net state variable." They define this as the smallest (true) value of the net state variable that gives a specified probability that the value of the response variable will exceed its critical value, i.e., that the material analyzed is not blank. The "minimum detectable activity

(MDA)" is similar, but relates to the quantity (activity) of a *radionuclide* rather than the concentration of a *radionuclide*.

mixed wastes**:** Regulated wastes containing both chemically hazardous and radiological materials.

monoenergetic: The quality of a particle or quantum of energy that has a discrete, well-defined energy range. This is a characteristic of emitted alpha particles and gamma- and X-rays.

net count rate: The value resulting from the subtraction of the background count rate, instrument background or appropriate blank from the total (gross) count rate of a source or sample.

nuclide**:** A general term for an atom with a given combination of protons, neutrons, and nuclear energy state. See *radionuclide* and *isotope*.

parent radionuclide**:** The initial *radionuclide* in a decay series that decays to form one or more *progeny*

Poisson distribution**:** The distribution of the total *radioactive* counts obtained over time as a result of fluctuations governed by the laws of probability, as is the case for the *radioactive* decay process.

positron**:** See *beta particle*.

progeny**:** One or more *radionuclides* that form from radioactive decay of a *parent radionuclide* in a decay series.

***quality assurance* (QA):** An integrated system of management activities involving planning, implementation, assessment, reporting, and quality improvement to ensure that a process, item, or service is of the type and quality needed and expected.

***quality control* (QC):** Monitoring key laboratory *performance indicators* as a means of determining if a laboratory's measurement processes are in control.

quality control samples**:** Samples analyzed for the purpose of assessing imprecision and bias.

quality indicators**:** Measurable attributes of the attainment of the necessary quality for a particular environmental decision. Precision, bias, completeness, and sensitivity are common data quality indicators for which quantitative MQOs could be developed during the planning process.

quality system**:** The *quality system* oversees the implementation of QC samples, documentation of QC sample compliance or noncompliance with MQOs, audits, surveillances, performance evaluation sample analyses, corrective actions, quality improvement, and reports to management.

radioactive**:** (1) the property possessed by some elements or isotopes of spontaneously emitting radiations by the transformation of their nucleus. (2) The product of nuclear transformations (disintegrations) in which the energy (or a fraction thereof) of the process is emitted in the form of alpha particles, beta particles, or photons. See *decay*.

radiochemical analysis**:** The analysis of a sample matrix for its *radionuclide* content, both qualitatively and quantitatively.

radiolysis**:** Chemical reactions, including decomposition, induced by radiation.

radionuclide**:** A species of atom characterized by its mass number, atomic number, and nuclear energy state, providing that the mean half-life in that state is long enough to be observable. The majority of known nuclides are *radioactive*. The term "radionuclide" is used when referring to a specific *radioactive* nuclide without relating it to other isotopes of an element.

radiotracer**:** (1) A radioactive isotope of the analyte that is added to the sample to measure any losses of the analyte during the chemical separations or other processes employed in the analysis (the chemical yield). (2) A radioactive element that is present in only extremely minute quantities, on the order of 10^{-15} to 10^{-11} Molar.

recovery**:** The actual amount of material detected in a *laboratory control sample* (LCS) or spiked sample, expressed in percent of the amount of material that was added. In an ideal situation, the result of an analysis of the *laboratory control sample* should be equivalent to (give 100 percent of) the target analyte concentration or activity known to be present in the fortified sample or standard material. The result normally is expressed as percent recovery. Because most radioanalytical methods use *radiotracers* or analyze a *radionuclide* in a sample without losses, recovery is a measure of method bias for repetitive measurements. The LCS recovery differs from the recovery of a matrix spike in that the matrix spike is added directly to the environmental sample and the percent recovery is determined by comparing the difference between the original and spiked samples after accounting for the activity in the original (unspiked) sample.

rem**:** The common unit for the effective or "equivalent" dose of radiation received by a living organism, equal to the actual dose (in rads) multiplied by a factor representing the danger of the radiation. "Rem" stands for "roentgen equivalent man," meaning that it measures the biological effects of ionizing radiation in humans. One rem is equal to 0.01 Sv. See *sievert*.

representativeness**:** (1) The term employed for the degree to which samples properly reflect their parent populations. (2) A representative sample is a sample collected in such a manner that it reflects one or more characteristics of interest (as defined by the project objectives) of a population from which it was collected. (3) One of the five principal data quality indicators (i.e., precision, bias, *representativeness*, comparability, and completeness).

reproducibility**:** A measure of laboratory precision based on each sample matrix. Duplicate or replicate sample results are used to evaluate *reproducibility* of the complete laboratory subsampling, preparation, and analytical process.

SAFSTOR**:** A method of decommissioning in which the nuclear facility is placed and maintained in such condition that the nuclear facility can be safely stored and subsequently decontaminated to levels that permit release for unrestricted use.

sievert **(Sv):** The SI unit for the effective dose of radiation received by a living organism. It is the actual dose received ("*grays*" in SI or "rads" in traditional units) times a factor that is larger for more dangerous forms of radiation. One sievert is 100 *rem*. Radiation doses are often measured in millisieverts (mSv). An effective dose of 1 Sv requires 1 *gray* of *beta* or *gamma* radiation but only 0.05 *gray* of *alpha* radiation or 0.1 *gray* of neutron radiation.

***spike*:** (Also termed "matrix spike.) A known amount of target analyte added to the environmental sample in order to establish if the method or procedure is appropriate for the analysis of the particular matrix and how the target analyte responds when the environmental sample is prepared and measured, thereby estimating the bias introduced by the sample matrix.

***standard uncertainty*:** The estimated standard deviation associated with a measured value. Statistically, the standard uncertainty of x is denoted by $u(x)$.

***uncertainty*:** The term "uncertainty" may have several shades of meaning. In general it refers to a lack of complete knowledge about something of interest. It usually refers to "uncertainty of measurement," which is a parameter associated with the result of a measurement that characterizes the dispersion of the values that could reasonably be attributed to the measurand. See also, *standard uncertainty*.

***X-rays*:** First discovered in 1895, X-rays are part of the electromagnetic spectrum, with wavelengths shorter than visible or radio waves. X-rays originate from the realignment of atomic shells (orbital electrons) during the decay process. While they exhibit the same dual behavior as light (waves and photons), and they can be polarized or refracted, they are capable of penetrating matter. See *gamma rays*.

Appendix B: Principles of Radioactive Decay and Radioactive Equilibrium

B.1 Introduction

This discussion on radioactivity and radiation provides the basic concepts of nuclides, radionuclides, radioactive decay, and decay emissions. These concepts are important to the measurement of radioactivity from samples. This fundamental knowledge, in addition to the historical site assessment, will assist the project managers in determining the scope of work that may originate from the various sites.

B.1.1 Nuclides

Elements may be differentiated by their physical and chemical characteristics. The elements are arranged within the Periodic Table according to the number of protons in their nucleus (atomic number, or "Z number"); all atoms of a particular element have the same number of protons. Individual elements may have more than one "isotope," which are atoms of an element that have the same number of protons (Z) but a different number of neutrons (N) in their nucleus. For example, in addition to the stable ^{27}Al, there are 14 other known isotopes of aluminum ranging in mass number between 22 and 35. For aluminum, these other 14 isotopes are radioactive or unstable nuclides. Other elements, such as iron (Fe), have several stable isotopes of different abundances (^{54}Fe – 5.8 percent, ^{56}Fe – 91.8 percent, ^{57}Fe – 2.1 percent, and ^{58}Fe – 0.3 percent) as well as radioactive isotopes. When referring to a radioactive isotope of an element, the term "radioisotope" often is used. Isotopes of a given element have the same chemical properties, whether they are radioactive or not. The ratio of Z to N determines the stability of the nucleus (i.e. whether or not the atom is radioactive).

The general term for a specific combination of Z and N is a "nuclide." The mass number (A) of the nuclide is the sum of the number of protons and neutrons (A = Z + N). The positive charge of the nucleus (Z^+) establishes the number of electrons in the neutral atom, and determines the configuration of the outermost electrons. This element-specific structure of the electron cloud of the neutral atom determines how the atom will ionize, and thus its chemical properties.

When writing a specific nuclide in symbolic form, the atomic number and mass are included. For example, the symbolic form of stable aluminum is $^{27}_{13}\mathrm{Al}$, which is the only stable nuclide (100 percent abundance) of aluminum. Common nomenclature normally does not include the Z number in the symbolic form because the element symbol (Al) uniquely represents the number of protons in the nucleus for that element— ^{27}Al.

Nuclides with the same atomic mass (Z + N) are called "isobars." For example, ^{36}Cl and ^{36}S, although chemically and physically different because of their different Z numbers, are isobars because their A values are the same.

B.1.2 Radionuclides

The majority of known nuclides are radioactive. The term "radionuclide" is used when referring to a specific radioactive nuclide without relating it to other isotopes of an element. The radioactive decay of each radionuclide is unique in terms of its mean time (or half-life) for decay and the nuclear emissions during the decay process. Radionuclides can be found in nature but most are generated by man-made nuclear reactions such as nuclear fission or activation. Naturally occurring radionuclides can be delineated into two groups according to their origin, primordial and cosmogenic. Primordial radionuclides are those nuclides that have been present since the formation of the Earth, and whose half-lives are sufficiently long to permit detection of these nuclides today. Examples of primordial nuclides are ^{238}U and ^{232}Th. In some cases, the primordial nuclides decay into a series of other shorter lived radionuclides (referred to as a “decay chain”). Cosmogenic radionuclides are those nuclides formed by the irradiation of stable elements, primarily in the atmosphere, by neutrons, gamma rays, or protons from solar irradiance. Cosmogenic radionuclides have half-lives that may be short or very long (^{7}Be and ^{14}C, respectively).

There are three long-lived, naturally occurring, radionuclides that are the “parents” of decay chains with numerous members: ^{238}U, ^{232}Th, and ^{235}U. An additional decay chain once existed from ^{237}Np ($t_{½} \approx 2.1 \times 10^6$ y), which has long since “died out,” because the half-lives of the parent and progeny are much shorter than the age of the Earth (about 4.6×10^9 y). The decay chains of the existing long-lived radionculides are depicted in Figures 3, 4, and 5.

B.1.3 Radioactive Decay

It has been recognized that a nuclide will be stable if it contains a certain combination of neutrons and protons. Of the known elements, only elements from hydrogen ($Z = 1$) to bismuth ($Z = 83$) have stable nuclides. Technetium (43) and promethium (61), however, are exceptions and have no stable isotopes. If one plots the number of protons (Z) against the number of neutrons (N), it becomes apparent that the stable nuclides form a “line of stability” with a slope of about one (or $N \approx Z$) for the first 20 elements and a slope of less than one (or $N > Z$) for higher Z elements. When a nuclide has too many neutrons, the nucleus is unstable, and a neutron will be converted to a proton resulting in β^- emission. An example of this is

$$^{60}_{27}\mathrm{Co} \xrightarrow{\beta^-} {}^{60}_{28}\mathrm{Ni}.$$

When a nuclide has too many protons, the nucleus is also unstable, and a proton is converted to a neutron either through a positron emission or capture of an orbital electron (electron capture). Examples of these changes include:

$$^{58}_{27}\mathrm{Co} \xrightarrow{\beta^+} {}^{58}_{26}\mathrm{Fe}$$

and

$$^{58}_{27}\mathrm{Co} \xrightarrow{e^-\ \text{capture}} {}^{58}_{26}\mathrm{Fe}$$

For nuclides that have a large excess of neutrons and protons, the nucleus can approach stability by emitting an alpha particle $\left({}^{4}_{2}\mathrm{He}^{+2}\right)$. Examples of an alpha emission that result in stable or unstable nuclides are:

$$^{212}_{84}\mathrm{Po} \xrightarrow{\alpha} {}^{208}_{82}\mathrm{Pb}\ \text{(stable)}$$

and

$$^{226}_{88}\mathrm{Ra} \xrightarrow{\alpha} {}^{222}_{86}\mathrm{Rn}\ \text{(unstable: radioactive)}$$

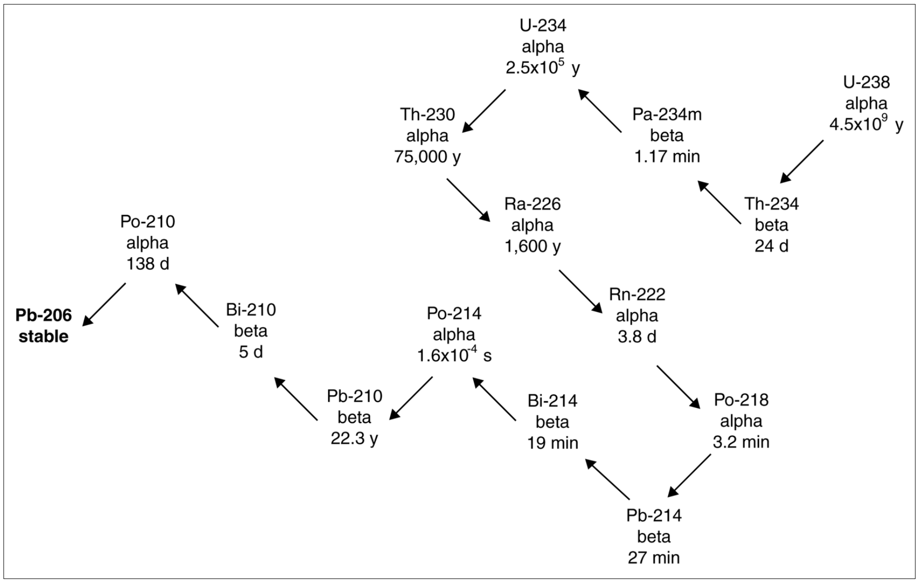


FIGURE 3 — Uranium-238 decay chain

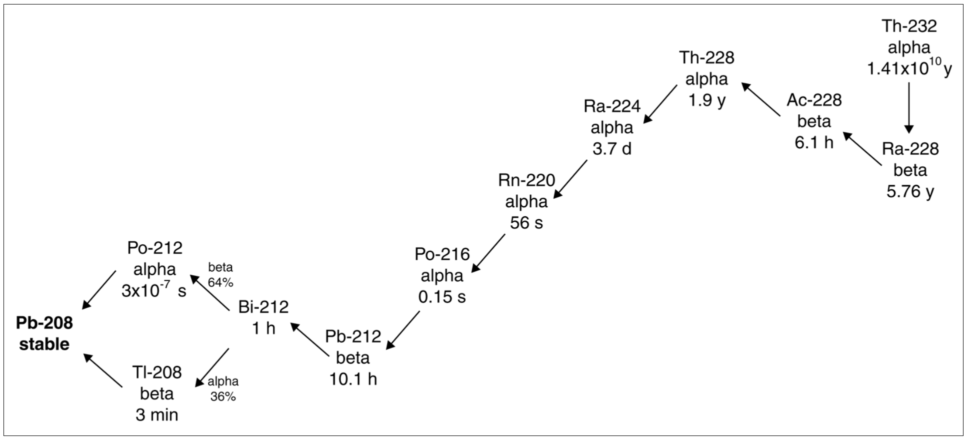


FIGURE 4 — Thorium-232 decay chain

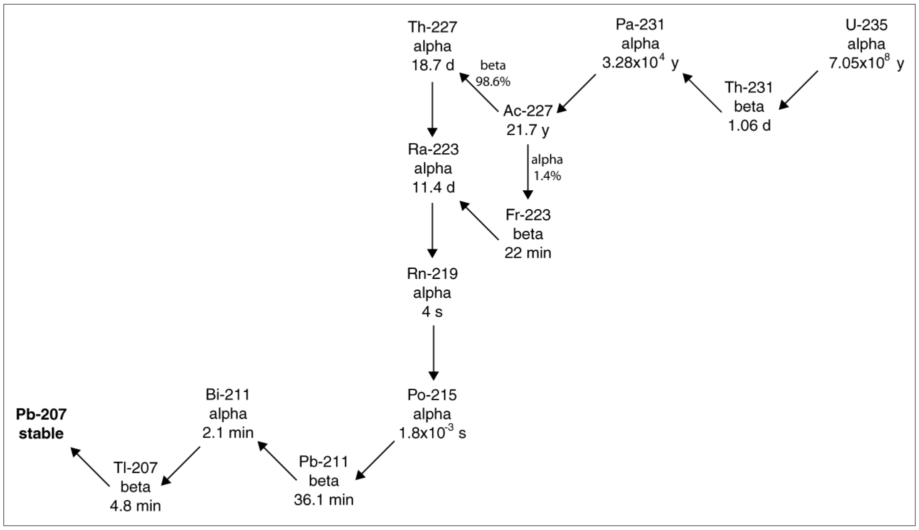


FIGURE 5 — Uranium-235 decay chain

During radioactive decay, the number of atoms (N) of a radionuclide decreases over time according to its own characteristic decay rate. Mathematically, the number of atoms decaying (dN) in a short time interval (dt) can be expressed as:

$$dN = -\lambda N \, dt$$

where λ is the decay constant for the radionuclide.

Integrating the differential equation results in the well-known radioactive decay equation:

$$N = N_0 e^{-\lambda(t-t_0)}$$

where: N is the number of radioactive atoms remaining at time t, and
N_0 is the initial number of atoms at time t_0.

There is an important relationship between the radionuclide's decay constant and its half-life. By definition, the half-life ($t_{½}$) of a radionuclide is the time interval needed to reduce the number of atoms by half. Simplifying the equation for λ with $N = ½N_0$ would result in $\lambda = [\log_e 2]/t_{½}$, or $\lambda = 0.6931/t_{½}$. In most reference materials on the properties of the various radionuclides, the half-life of the radionuclide will be specified, typically in units of years (y), days (d), hours (h), minutes (m) or seconds (s). The λ is expressed in reciprocal time units; y^{-1}, d^{-1}, h^{-1}, min^{-1}, or s^{-1}.

Most radioactive measurements deal with activity or the number of atoms decaying per unit of time. A radionuclide's activity is calculated by the equation $A = N\lambda$. The new unit of radioactivity is the becquerel (Bq), and is defined as one disintegration (decay) per second. The more common unit is the picocurie (pCi) or 10^{-12} Ci, which equals 2.22 disintegrations per minute (dpm), or 0.037 Bq. For example, 500 Bq of ^{60}Co will decay to 250 Bq in one half-life ($t_{½} \approx 5.27$ y).

B.1.4 Radioactive Decay Emissions

Unstable nuclides (radionuclides) decay randomly to stable and unstable nuclides of lower atomic mass. The difference between the masses of the original nuclide, and the decay product (progeny) nuclide is related to the radiation emitted during the decay process according to Einstein's famous mass-energy equation, $E = mc^2$.

Emissions from the nucleus of an atom during radioactive decay that are important to the measurement of radioactivity in samples include alpha particles, beta particles (as β^- or β^+), gamma rays, and X-rays (which also may be emitted as a result of electron capture and other nuclear phenomena). The energy of these emissions is stated in terms of electron volts (eV), which is equivalent to 1.6×10^{-12} erg. Energies of alpha and beta particles are generally expressed in MeV while that for gamma- and X-rays are expressed in keV.

B.1.4.1 Alpha Particles

An alpha particle (α) is the heaviest particle emitted during radioactive decay (heavier particles can occur but are rare). An α particle is essentially a helium nucleus, comprised of two protons and two neutrons ($Z = 2$, $A = 4$). When ejected from the nucleus of a heavier unstable atom during radioactive decay ("alpha emission"), it always has a discrete energy ("monoenergetic"). However, the decay process may emit an alpha particle of one of several possible discrete energies, each with a probability of emission per decay. For example, for ^{241}Am, an alpha particle emission may have one of three energies, each with a different probability of emission: 5.486 MeV (85.2 percent probability), 5.443 MeV (12.8 percent), and 5.388 MeV (1.4 percent). The "signature" of an alpha emitting radionuclide is its alpha particle energy. This energy signature, along with the nuclide's half-life, are specific to the identification of an alpha-emitting radionuclide. For example, the alpha energy of ^{210}Po ($t_{½} \approx$ 138 d) is 5.305 MeV, while the alpha energy of ^{208}Po ($t_{½} \approx$ 2.90 y) is 5.116 MeV. Typically, the shorter the half-life, the greater the energy of the alpha particle.

When interacting with materials, alpha particles have a very short penetration range and travel in a nearly a straight manner, i.e., with minimal scattering. This is especially important when detecting alpha particle emissions from radionuclides isolated by radiochemical means. A 5 MeV alpha particle has a range of about 3.5 cm in air and 0.03 mm in skin or water. As such, test sources containing alpha-emitting radionuclides must be extremely thin for proper detection and energy identification, typically in the micron thickness range. It should be noted that particle and photon absorption thickness are stated in units of milligrams per square centimeter (mg/cm^2), which for particles is equivalent to the range (cm) times density of material (g/cm^3).

B.1.4.2 Beta Particles, Positrons, and Conversion Electrons

Beta particles (β^-) and positrons (β^+) originate in the nucleus of an atom, while a conversion electron is generated from the interaction of a gamma ray with an orbital electron. All of these particles have the same mass, but the beta and conversion electrons (β^- and e^-) have a negative charge while the positron has a positive charge. The charge of a β^-, β^+, and e^- is 1.602×10^{-19} Coulombs. Like α particles, conversion electrons are monoenergetic, having the energy of the gamma ray minus the energy needed to remove the electron from orbit. The emissions of beta particles and positrons always have an energy distribution from zero to a maximum, $E_{\beta\max}$, with an average of approximately ⅓ $E_{\beta\max}$.

Because an electron has a low mass and a single charge, it is more easily scattered and less readily absorbed in materials compared to other nuclear particles such as alphas and protons. In addition, as a result of this scattering, an electron's path through material is nonlinear and tortuous. Absorption of β^-, β^+, and e^- in materials is relatively independent of the atomic number of the material. However, their absorption range varies according to the density of the material. For energies above one MeV, the range of a β^- and β^+ is linear with respect to energy (Lapp and Andrews, 1964). The range of a tritium beta particle of $E_{\beta\max}$ = 0.018 MeV is 0.6 mg/cm^2 (6 µm in water), while the range for a ^{32}P beta particle of $E_{\beta\max}$ = 1.71 MeV is 800 mg/cm^2 (8 mm in water). Different radiation detection methodologies are used for low energy (< 0.200 MeV) β^-, β^+, and e^- compared to those of medium to high energy.

B.1.4.3 X-Rays, Gamma Rays, and *Bremsstrahlung* Radiation

X- and gamma (γ) rays are electromagnetic radiations that have defined energies. X-rays originate from the realignment of atomic shells (orbital electrons) during the decay process. One requirement for an X-ray emission is the creation of an electron vacancy in an inner shell. Because there are many electron shells for atoms of atomic number greater than 10 (neon), there is a probability that the X-rays from a radioactive decay will have more than one energy. However, the energy of an X-ray is always smaller than the highest electron-binding energy in atomic shells or under about 100 keV. The probability of an X-ray emission of a specific energy per atomic disintegration has been determined and is listed with the characteristic of the radionuclide.

Gamma rays originate from the nucleus of an atom as a result of nuclear de-excitation and have energies from about 20 keV to several MeV. Following α, β^-, or β^+ emission, the nucleus may still have excess energy; this energy is released in the form of gamma rays. Gamma rays are more probable with β^- and β^+ emissions than with α emissions. Gamma-ray emission, without accompanying particle emission, is known as “isomeric transition” (the nucleus goes from an excited state to a ground state). The discrete energies of the X- and γ-rays are used to identify the radionuclides from which they originated.

For a laboratory application, *bremsstrahlung* radiation is produced whenever electrons (β^- and β^+) are decelerated in matter. Unlike X- and γ-rays, *bremsstrahlung* radiation shows a continuous spectrum of photon energy extending from zero to the maximum energy ($E_{\beta\max}$) of the β^- or β^+. There are only a few radioanalytical methods that use *bremsstrahlung* radiation detection as a means to quantify a radionuclide.

The degree of interaction of photons, such as X-, γ-, and *bremsstrahlung* radiations, is highly dependent on the photon energy. Gamma-rays, which have energies typically > 100 keV, are more penetrating and are less absorbed by matter compared to lower energy X-rays (typically less than 100 keV). This is an important characteristic when choosing a radiation detector and for shielding detectors from photons originating from outside (external background radiations) the sample being analyzed. For most remediation sample analyses, gamma-ray detectors are typically shielded with a minimum of 102 mm of lead or other very dense material.

B.1.5 Techniques for Radionuclide Detection

When there is sufficient activity, the detection and identification of a specific radionuclide is accomplished by evaluating the radiological and chemical properties of the nuclide of interest. For radionuclides that emit characteristic gamma rays of a specific energy, the detection and identification of the nuclide is based on the radiological characteristics only. For nuclides that emit beta and alpha particles, a combination of radiological and chemical characteristics may be needed to identify and quantify the nuclide of interest. In these cases, the nuclide is isolated from the sample matrix through chemical means and then concentrated in some final chemical form (e.g., $^{89}SrCO_3$) used as a test source. The resulting test source can be analyzed by either a beta or alpha detector depending on the nuclide’s decay scheme or particle emission. In some cases, where there may be several isotopes of the element in the test source, a particle energy spectrometry measurement is necessary to discern the various isotopes, e.g., ^{238}Pu and ^{239}Pu. Also, radioanalytical methodologies may employ chemical separation schemes and detectors that are specific to identifying and quantifying a radioactive decay product of the nuclide of interest. Examples of this type of methodology application include separating and analyzing ^{90}Y, the short lived ($t_{½} \approx 64.0$ h) decay of ^{90}Sr and the collection and analysis of ^{222}Rn ($t_{½} \approx 3.82$ d), the first decay product of ^{226}Ra.

Radiation detection methodologies have been developed based on the physical interaction of the decay emissions with special materials that have certain characteristics that may be measured following the absorption of the radiation. Radiation detectors may be based on the following physical principles: ionization of gases, creation of electron-hole pairs in semiconductor materials, and the change of energy states with subsequent light emissions for certain organic and inorganic materials. Examples of these radiation detection methodologies include gas proportional counting for α and β detection, large germanium and silicon semiconductor detectors for X- and γ-ray detection and spectrometry, silicon semiconductor detectors for α spectrometry, and organic liquid scintillation counting for low-energy β particles and limited α spectrometry.

B.1.6 Radioactive Equilibrium

When the decay product of a radionuclide is another radionuclide, three distinct cases—referred to as "radioactive equilibria"—may be derived mathematically. These are based on the relationship of the half-lives of the original and newly formed radionuclide. These cases are referred to as secular, transient, and no equilibrium, and the relationship is referred to as "parent-progeny" (Friedlander et al., 1981). Thus, radioactive equilibrium may be described as the relative proportion of the activity of each of two or more radionuclides.

These relationships become complex when the progeny gives rise to a nuclide 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 will be present eventually as the predecessor radionuclides undergo radioactive decay. Examples of these chains are:

SECULAR EQUILIBRIUM
Decay-chain nuclides: ^{238}U ➛ ^{234}Th ➛ ^{234m}Pa ➛ *many others*
Half-lives: 4.47×10^9 y 24.1 d 1.2 min

TRANSIENT EQUILIBRIUM
Decay-chain nuclides: ^{95}Zr ➛ ^{95}Nb
Half-lives: 64 d 35 d

NO EQUILIBRIUM
Decay-chain nuclides: ^{210}Bi ➛ ^{210}Po ➛ ^{206}Pb (stable)
Half-lives: 5 d 1.38×10^2 d

The relationship expressing the number of atoms of each of the radionuclides present in a decay chain after a certain period of time has elapsed can be expressed by the Batemann Equation (Friedlander et al., 1981). If a quantity of the parent is chemically isolated, the amount of each progeny can be calculated for any time period after the time of separation. For environmental samples, the secular and transient equilibria are most significant because the parent radionuclide has a long half-life, and the progeny have relatively short half-lives or a shorter half-life than the parent. In many cases, if the progeny were present all by themselves, they would decay and might not be detected. But because of the decay chain relationship, new progeny continue to be formed by the parent. Thus, it appears that the half-life of the progeny is the same as that of the parent.

However, in the environment, this decay equilibrium can be upset because of the different chemical properties of each of the radionuclides in the decay chain. Figure 6 shows an example of how this upset to the radioactive equilibrium can occur. Initially the ^{232}Th and ^{228}Ra and ^{238}U and ^{226}Ra (from two separate radioactive decay chains), establish a radioactive equilibrium with their respective progeny, radium and radon. These radioactive equilibria initially occur in their respective media. Thorium does not dissolve in water (indicated by the "X" over that arrow), while radium does. As the radium dissolves, it is only partially "supported" in the water, because the thorium does not dissolve.

The other decay chain has ^{226}Ra as the fifth progeny of ^{238}U. Because uranium is more soluble than thorium, the decay chain in the liquid phase is fed continually by its parent. Initially, it is in radioactive equilibrium with the radium and radon decay products in water. The ^{226}Ra is fully supported. However, due to the volatility of radon, it escapes the water column and is "unsupported" in air by radium because radium is not volatile (also indicated by the "X" over that transition). When radon is volatilized from water, but radium is not, the radon in the water is not completely supported; there is a loss of radon to the *air*, but radium keeps feeding the radon to the *water*. In each case where the progeny are less than fully supported, there will be an indeterminable or nonexistent radioactive equilibrium. Samples with radionuclides that are partially or fully unsupported need special attention when establishing the time from sampling to analysis, because in some instances the radionuclide of interest may decay away before analysis can occur.

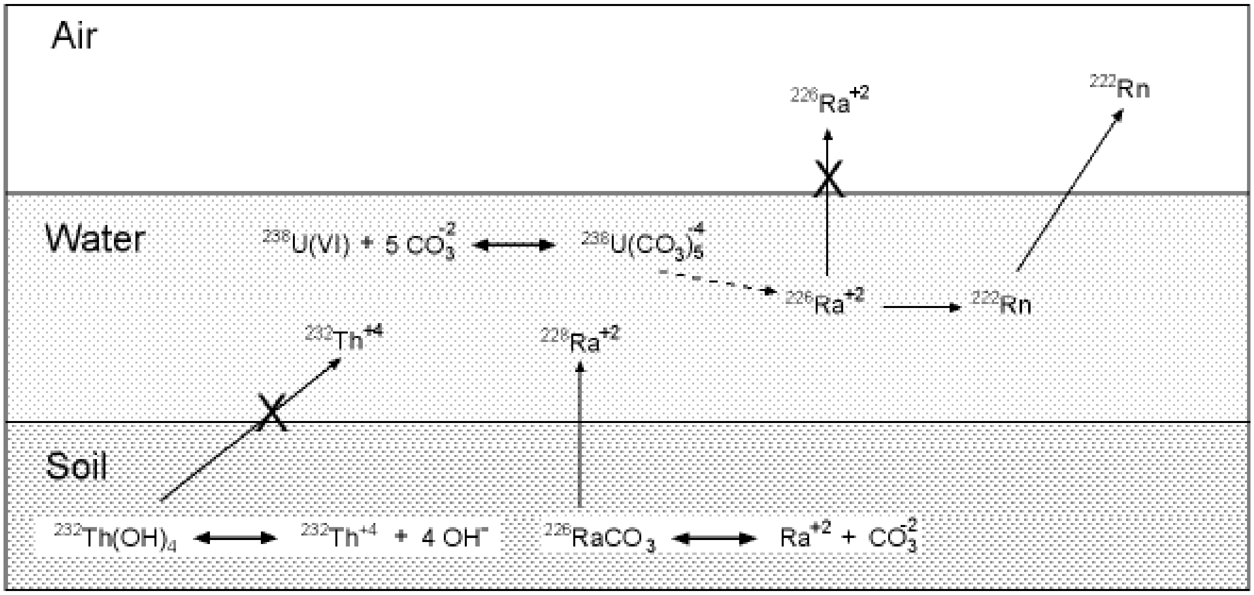


FIGURE 6 — Environmental and chemical factors affecting radioactive equilibrium

Similar cases of radionuclide progeny being unsupported in an environmental medium hold true for other radionuclides discussed in this document such as plutonium, americium, and lead.

B.1.7 Useful Websites and Sources for Background Information on Radioactivity

- Units of measure: www.physics.nist.gov/cuu/index.html
- Table of nuclides: http://atom.kaeri.re.kr/ton/
- Periodic chart of the elements: www.webelements.com

The following websites can be used to access technical reference material such as nuclide decay schemes, half-lives, and decay emissions:

- All nuclides; National Nuclear Data Center:
  www.nndc.bnl.gov
  www.nndc.bnl.gov/nndc/ensdf/

- Nuclides typical for natural background and environmental remediation; DHS Environment Measurements Laboratory, EML Publications, Procedure Manual (HASL 300), Chapter 5 Radionuclide Data: www.eml.st.dhs.gov/publications/procman/.

- Gamma-ray spectra and decay schemes: www.inl.gov/gammaray/catalogs/index.shtml

- Radiochemical processes: library.lanl.gov/radiochemistry/elements.htm

- Statistical applications to measurements including process control:
  www.itl.nist.gov/div898/handbook/index2.htm
  ie.lbl.gov/toi/
  www.inl.gov/gammaray/links.shtml

- Federal Radiological Monitoring and Assessment Center (FRMAC):
  www.nv.doe.gov.nationalsecurity/homelandsecurity/frmac/default.htm

Appendix C: Radionuclide Parameters and Characteristics

Radionuclide	Decay Mode	Half-Life	Means of Production	DOE*	NPP	NORM
^{241}Am	α, γ	423 y	Activation	✔	✔	
^{243}Am	α, γ	7.37×10^{3} y	Activation	✔		
^{210}Bi	β	5.0 d	Natural decay of ^{238}U	✔		✔
^{14}C	β	5.72×10^{3} y	Cosmic Radiation, activation	✔	✔	
^{134}Cs	β, γ	2.0 y	Fission	✔	✔	
^{137}Cs	β, γ	30 y	Fission	✔	✔	
^{60}Co	β, γ	5.3 y	Activation	✔	✔	
^{3}H	β	12.3 y	Cosmic radiation, fission	✔	✔	
^{125}I	ε, γ	59.4 d	Accelerator	✔		
^{129}I	β, γ	1.6×10^{7} y	Fission	✔	✔	
^{131}I	β, γ	8.0 d	Accelerator, fission	✔	✔	
^{192}Ir	β, γ	73.8 d	Activation	✔		
^{210}Pb	β, γ	22.6 y	Natural decay of ^{238}U			✔
^{59}Ni	ε	7.6×10^{4} y	Activation	✔	✔	
^{63}Ni	β	100 y	Activation	✔	✔	
^{32}P	β	14.3 d	Accelerator	✔	✔	
^{238}Pu	α	87.7 y	Activation	✔	✔	
^{239}Pu	α	2.4×10^{4} y	Activation	✔	✔	
^{240}Pu	α	6.6×10^{3} y	Activation	✔	✔	
^{241}Pu	β, α	14.4 y	Activation	✔	✔	
^{226}Ra	α	1.6×10^{3} y	Natural decay of ^{238}U			✔
^{228}Ra	β	5.8 y	Natural decay of ^{232}Th			✔
^{89}Sr	β	50.5 d	Fission	✔	✔	
^{90}Sr	β	28.8 y	Fission	✔	✔	
^{35}S	β	87.2 d	Accelerator	✔	✔	
^{99}Tc	β	2.1×10^{5} y	Fission, accelerator	✔	✔	
^{227}Th	α, γ	18.7 d	Natural decay of ^{235}U	✔		✔
^{228}Th	α, γ	1.9 y	Natural decay of ^{232}Th			✔
^{230}Th	α, γ	7.5×10^{4} y	Natural decay of ^{238}U	✔		✔
^{232}Th	α	1.4×10^{10} y	Primordial			✔
^{234}U	α	2.4×10^{5} y	Natural decay of ^{238}U	✔		✔
^{235}U	α, γ	7.0×10^{8} y	Primordial	✔	✔	✔
^{238}U	α	4.5×10^{9} y	Primordial	✔	✔	✔

* DOE — Department of Energy site cleanup activities
NORM — Naturally occurring radioactive materials waste
NPP — Nuclear power plant site decommissioning

Appendix D: Tables of Radioanalysis Parameters

Page

The following tables identify many analytical parameters for the radionuclides discussed in this document. The column labeled "Typical MDC" refers to minimum detectable values that can reasonably be achieved with each type of instrument based on the listed sample size and count time. Other factors, such as instrument efficiency and detector background, play an important part in what the lowest achievable detection level will be with a particular instrument. Note that the values listed in these tables as "Typical MDC" are *below* any required MDC values that may be listed by EPA.

TABLE 1 — Americium

Matrix	Method (a)	Analyte	Half-Life (years)	Primary Energy of Detected Particle (b)	Chemical Separation (Y/N)	Sample Size	Typical MDC (c)	Total Analysis Time (days) (d)	Count Time (Hours)	Interfering Materials	Source (e)
Water						liters	pCi/L				
	GS	241	433	γ, 0.0595	N	1.0	20	1 – 1.5	20 – 24	Compton background from higher-energy γ-rays	NPP, DOE
	GS	241	433	γ, 0.0595	N	1.0	54 (f)	0.5	0.1	Compton background from higher-energy γ-rays	
	AS	241	433	α, 5.486	Y	0.05	0.2	1 – 2	16 – 24	Pu-238	NPP, DOE
	AS	241	433	α, 5.486	Y	0.05	54 (f)	1	2– 4	Pu-238	
	AS	243	7370	α, 5.276	Y	0.05	0.5	1 – 2	16 – 24		DOE
	GP	241	433	α, 5.486	Y	0.1	0.5	1 – 2	16 – 24	Pu-238	NPP, DOE
	GP	241	433	α, 5.486	Y	0.1	54 (f)	1	2– 4	Pu-238	
Soil						grams	pCi/g				
	GS	241	433	γ, 0.0595	N	100	0.75	1 – 1.5	16 – 24	1. Self-absorption by sample 2. Compton background from higher-energy γ-rays	NPP, DOE
	GS	241	433	γ, 0.0595	N	100	917	0.5	0.1	1. Self-absorption by sample 2. Compton background from higher-energy γ-rays	
	AS	241	433	α, 5.486	Y	0.5	0.1	4 – 5	16 – 24	Pu-238	NPP, DOE
	AS	241	433	α, 5.486	Y	5	917	2 – 3	16 – 24	Pu-238	
	AS	243	7370	α, 5.276	Y	5	0.5	4 – 5	16 – 24		NPP, DOE
	GP	241	433	α, 5.486	Y	10	0.01	4 – 5	16 – 24		NPP, DOE
	GP	241	433	α, 5.486	Y	10	917	2 – 3	2 – 4		

Notes:

a. Method descriptions in Section 4.1
b. Units are MeV for decay particles, N/A for atom count methods (see Section 3.10)
c. Typical MDCs for NPP and DOE based on sample size and count time; see discussion in Section 3.3 and box on page 80
d. Time required to generate final data in laboratory (excluding data report generation or any QC validation)
e. Source as noted in Section 1.1
f. MDC for Am-241 in water represents the sum of Am-241, Pu-238, and Pu-239/240

Alpha Spectrometry (AS), Accelerator Mass Spectrometry (AMS), Gas Flow Proportional Counting (GP), Gamma Spectrometry (GS), Inductively Coupled Plasma-Mass Spectrometric Analysis (ICP-MS), Kinetic Phosphorescence Analysis (KPA), Liquid Scintillation Counting (LSC), Thermal Ionization Mass Spectrometry (TIMS), Photon-Electron Rejecting Alpha Liquid Scintillation (PERALS®)

TABLE 2 — Bismuth

Matrix	Method (a)	Analyte	Half-Life (days)	Primary Energy of Detected Particle (b)	Chemical Separation (Y/N)	Sample Size	Typical MDC (c)	Total Analysis Time (days) (d)	Count Time (Hours)	Interfering Materials	Source (e)
Water						liters	pCi/L				
	GP	210	5.01	β, 1.162	Y	1.0	0.5	2 – 3	10 – 16		NORM
	LSC	210	5.01	β, 1.1623	Y	0.1	0.3	2 – 3	10 – 16		NORM
Soil						grams	pCi/g				
	GP	210	5.01	β, 1.162	Y	1	0.05	2 – 3	10 – 20		NORM
	LSC	210	5.01	β, 1.162	Y	1	0.5	2 – 3	4 – 5		NORM

Notes: (All beta-particle energies are beta maximums)

a. Method descriptions in Section 4.1

b. Units are MeV for decay particles, N/A for atom count methods (see Section 3.10)

c. Typical MDCs for NORM based on sample size and count time; see discussion in Section 3.3 and box on page 80

d. Time required to generate final data in laboratory (excluding data report generation or any QC validation)

e. Source as noted in Section 1.1

Alpha Spectrometry (AS), Accelerator Mass Spectrometry (AMS), Gas Flow Proportional Counting (GP), Gamma Spectrometry (GS), Inductively Coupled Plasma-Mass Spectrometric Analysis (ICP-MS), Kinetic Phosphorescence Analysis (KPA), Liquid Scintillation Counting (LSC), Thermal Ionization Mass Spectrometry (TIMS), Photon-Electron Rejecting Alpha Liquid Scintillation (PERALS®)

TABLE 3 — Carbon

Matrix	Method (a)	Analyte	Half-Life (years)	Primary Energy of Detected Particle (b)	Chemical Separation (Y/N)	Sample Size	Typical MDC (c)	Total Analysis Time (days) (d)	Count Time (Hours)	Interfering Materials (f)	Source (e)
Water						liters	pCi/L				
	LS	14	5,715	β, 0.157	Y	0.05	100	3	4 – 6		NPP, DOE
	GPC	14	5,715	β, 0.157	Y	0.1	100	4	4 – 6	Final sample thickness	NPP, DOE
Soil						grams	pCi/g				
	LS	14	5,715	β, 0.157	Y	5	0.2	5	4 – 6		NPP, DOE
	GPC	14	5,715	β, 0.157	Y	5	4	5	4 – 6	Final sample thickness	NPP, DOE
	AMS	14	5,715	N/A	N	0.001 (f)	0.01 (f)	2	0.5		NPP, DOE

Notes: (All beta-particle energies are beta maximums)

a. Method descriptions in Section 4.1

b. Units are MeV for decay particles, N/A for atom count methods (see Section 3.10)

c. Typical MDCs for NPP and DOE based on sample size and count time; see discussion in Section 3.3 and box on page 80

d. Time required to generate final data in laboratory (excluding data report generation or any QC validation)

e. Source as noted in Section 1.1

f. Value for minimum total carbon in the sample; the sample size should be based on achieving this much total carbon. If there was 0.001 g of carbon in a 1 g sample, the achievable MDC would be about 10 (Ognibene et al., 2003).

Alpha Spectrometry (AS), Accelerator Mass Spectrometry (AMS), Gas Flow Proportional Counting (GP), Gamma Spectrometry (GS), Inductively Coupled Plasma-Mass Spectrometric Analysis (ICP-MS), Kinetic Phosphorescence Analysis (KPA), Liquid Scintillation Counting (LSC), Thermal Ionization Mass Spectrometry (TIMS), Photon-Electron Rejecting Alpha Liquid Scintillation (PERALS®)

TABLE 4 — Cesium

Matrix	Method (a)	Analyte	Half-Life (years)	Primary Energy of Detected Particle (b)	Chemical Separation (Y/N)	Sample Size	Typical MDC (c)	Total Analysis Time (days) (d)	Count Time (Hours)	Interfering Materials (e)	Source (f)
Water						liters	pCi/L				
	GS	134	2.065	γ, 0.605	N	4	5 – 15	1–	6	Co-58, Sb-125, Coincidence sum	NPP, DOE
	GS	137	30.07	γ, 0.662	N	4	5 – 15	1	6	Ag-110m, Co-60, Single escape peak	NPP, DOE
	GS	134	2.065	γ, 0.605	N	4	32,000 (g)	0.1	0.2	Co-58, Sb-125, Coincidence sum	
	GS	137	30.07	γ, 0.662	N	4	32,000 (g)	0.1	0.2	Ag-110m, Co-60, Single escape peak	
Soil						grams	pCi/g				
	GS	134	2.065	γ, 0.605	N	100	0.1	1	3	Co-58, Sb-125, Coincidence sum	NPP, DOE
	GS	137	30.07	γ, 0.662	N	100	0.05	1	3	Ag-110m, Co-60, Single escape peak	NPP, DOE
	GS	134	2.065	γ, 0.605	N	100	—	0.1	0.1	Co-58, Sb-125, Coincidence sum	
	GS	137	30.07	γ, 0.662	N	100	55,560	0.1	0.1	Ag-110m, Co-60, Single escape peak	

Notes:

a. Method descriptions in Section 4.1
b. Units are MeV for decay particles, N/A for atom count methods (see Section 3.10)
c. Typical MDCs for NPP and DOE based on sample size and count time; see discussion in Section 3.3 and box on page 80
d. Time required to generate final data in laboratory (excluding data report generation or any QC validation)
e. Cs-134 activity will be underestimated unless correction is made specifically for coincidence-sum effects.
f. Source as noted in Section 1.1
G. MDC in water is for combined Cs-134 and Cs-137

Alpha Spectrometry (AS), Accelerator Mass Spectrometry (AMS), Gas Flow Proportional Counting (GP), Gamma Spectrometry (GS), Inductively Coupled Plasma-Mass Spectrometric Analysis (ICP-MS), Kinetic Phosphorescence Analysis (KPA), Liquid Scintillation Counting (LSC), Thermal Ionization Mass Spectrometry (TIMS), Photon-Electron Rejecting Alpha Liquid Scintillation (PERALS®)

TABLE 5 — Cobalt

Matrix	Method (a)	Analyte	Half-Life (years)	Primary Energy of Detected Particle (b)	Chemical Separation (Y/N)	Sample Size	Typical MDC (c)	Total Analysis Time (days) (d)	Count Time (Hours)	Interfering Materials	Source (e)
Water						liters	pCi/L				
	GS	60	5.271	γ, 1.332, 1.173	N	4	5	1	6		NPP, DOE
	GS	60	5.271	γ, 1.332, 1.173	N	4	—	0.2	0.5		
Soil						grams	pCi/g				
	GS	60	5.271	γ, 1.332, 1.173	N	100	0.1	1	6		NPP, DOE
	GS	60	5.271	γ, 1.332, 1.173	N	100	13,100	0.1	0.25		

Notes:

a. Method descriptions in Section 4.1
b. Units are MeV for decay particles, N/A for atom count methods (see Section 3.10)
c. Typical MDCs for NPP and DOE based on sample size and count time; see discussion in Section 3.3 and box on page 80
d. Time required to generate final data in laboratory (excluding data report generation or any QC validation)
e. Source as noted in Section 1.1

Alpha Spectrometry (AS), Accelerator Mass Spectrometry (AMS), Gas Flow Proportional Counting (GP), Gamma Spectrometry (GS), Inductively Coupled Plasma-Mass Spectrometric Analysis (ICP-MS), Kinetic Phosphorescence Analysis (KPA), Liquid Scintillation Counting (LSC), Thermal Ionization Mass Spectrometry (TIMS), Photon-Electron Rejecting Alpha Liquid Scintillation (PERALS®)

TABLE 6 — Hydrogen (Tritium)

Matrix	Method (a)	Analyte	Half-Life (years)	Primary Energy of Detected Particle (b)	Chemical Separation (Y/N)	Sample Size	Typical MDC (c)	Total Analysis Time (days) (d)	Count Time (Hours)	Interfering Materials	Source (e)
Water						liters	pCi/L (f)				
	LSC	3	12.3	β, 0.018	N	0.005	300	0.3	2	Colored matter, turbidity	NPP, DOE
	LSC	3	12.3	β, 0.018	Y (electrolysis)	0.05	5.0	5.0	2	Electrophilic compounds	NPP, DOE
	LSC	3	12.3	β, 0.018	γ	0.005	200	0.4	2		NPP, DOE
	ICP-MS	3	12.3	N/A	N	0.015	100	1	1		NPP, DOE
	ICP-MS (g)	He-3	12.3	N/A	N	0.015	100	1	1		NPP, DOE
Soil						grams	pCi/g				
	LSC	3	12.3	β, 0.018	N	100	0.05	1	5	Colored matter, turbidity, electrophilic compounds	NPP, DOE

Notes: (All beta-particle energies are beta maximums)

a. Method descriptions in Section 4.1

b. Units are MeV for decay particles, N/A for atom count methods (see Section 3.10)

c. Typical MDCs for NPP DOE based on sample size and count time; see discussion in Section 3.3 and box on page 80

d. Time required to generate final data in laboratory (excluding data report generation or any QC validation)

e. Source as noted in Section 1.1

f. Typical MDC is limited by levels of naturally occurring tritium in water at 50 pCi/L

g. This ICP-MS method counts the number of tritium-progeny atoms (^{3}He)

Alpha Spectrometry (AS), Accelerator Mass Spectrometry (AMS), Gas Flow Proportional Counting (GP), Gamma Spectrometry (GS), Inductively Coupled Plasma-Mass Spectrometric Analysis (ICP-MS), Kinetic Phosphorescence Analysis (KPA), Liquid Scintillation Counting (LSC), Thermal Ionization Mass Spectrometry (TIMS), Photon-Electron Rejecting Alpha Liquid Scintillation (PERALS®)

TABLE 7 — Iodine

Matrix	Method (a)	Analyte	Half-Life	Primary Energy of Detected Particle (b)	Chemical Separation (Y/N)	Sample Size	Typical MDC (c)	Total Analysis Time (days) (d)	Count Time (Hours)	Interfering Materials	Source (e, f)
Water						liters	pCi/L				
	GS (LEGe)	125	59.4 d	X-ray, 0.0355, 0.029	Y	1	(h)	2 – 3	2 – 4		DOE
	GS (LEGe)	129	1.57 × 10^7 y	X-ray, 0.0396, 0.0298	Y	1	20	2 – 3	2 – 4		NPP, DOE
	GS (LEGe)	129	1.57 × 107 y	X-ray, 0.0396, 0.0298	Y	1	1,500	0.5	1		
	GS	131	8.02 d	X-ray, 0.365	N	4	50	0.1	3	Compton background	NPP
	GP	131	8.02 d	β	Y	1	1.0	2	2 – 4		NPP, DOE
	LSC	129	1.57 × 10^7 y	β^-, 0.15	Y	1	50	2 – 3	3 – 4	C-14	NPP, DOE
	LSC	131	8.02 d	β^-, 0.606	Y	1	0.5	2 – 3	3		NPP
	LSC	129	1.57 × 10^7 y	β^-, 0.15	Y	1	1,500	2	2	C-14	
	ICP-MS	129	1.57 × 10^7 y	N/A	N	0.05	0.02	0.5	.5		NPP, DOE
Soil						grams	pCi/g				
	GS (LEGe)	125	59.4 d	X-ray, 0.0355, 0.029	Y	50	(h)	2 – 3	2 – 4		DOE
	GS (LEGe)	129	1.57 × 10^7 y	X-ray, 0.0396	Y	50	1	3 – 4	2 – 4		NPP, DOE
	GS	131	8.02 d	X-ray, 0.365	N	50	10 (g)	0.1	1.2	Compton background	NPP
	LSC	129	1.57 × 10^7 y	β^-, 0.15	Y	50	400	2 – 3	3 – 4	C-14	NPP, DOE
	AMS	129	1.57 × 10^7 y	N/A	N	0.001 (i)	0.001 (i)	0.5	0.5		NPP, DOE

Notes: (All beta-particle energies are beta maximums)

a. Method descriptions in Section 4.1
b. Units are MeV for decay particles, N/A for atom count methods (see Section 3.10)
c. Typical MDCs for NPP DOE based on sample size and count time; see discussion in Section 3.3 and box on page 80.
d. Time required to generate final data in laboratory (excluding data report generation or any QC validation)
e. Source as noted in Section 1.1
f. I-131 also has many commercial and medical applications outside NPP and DOE facilities
g. MDC is for NPP site. Due to the short half-life of I-131, the typical MDC could be an order of magnitude higher.
h. The activity of I-125 usually is relatively high, so most laboratories do not identify an MDC for this radionuclide. However, based on detector characteristics for a LEGE, the large yield for the iodine X-ray, and chemical separation concentration factors, MDC is estimated at 10 pCi/L and 1 pCi/g for water and soil, respectively.
i. The value of 0.001 represents the mass of stable I-127 in the sample required to achieve the detection limit of 10^{-3} pCi/g.

Alpha Spectrometry (AS), Accelerator Mass Spectrometry (AMS), Gas Flow Proportional Counting (GP), Gamma Spectrometry (GS), Inductively Coupled Plasma-Mass Spectrometric Analysis (ICP-MS), Low-Energy Germanium (LEGe), Kinetic Phosphorescence Analysis (KPA), Liquid Scintillation Counting (LSC), Reverse-Energy Germanium (REGe), Thermal Ionization Mass Spectrometry (TIMS), Photon-Electron Rejecting Alpha Liquid Scintillation (PERALS®)

TABLE 8 — Iridium

Matrix	Method (a)	Analyte	Half-Life (days)	Primary Energy of Detected Particle (b)	Chemical Separation (Y/N)	Sample Size	Typical MDC (c)	Total Analysis Time (days) (d)	Count Time (Hours)	Interfering Materials	Source (e, f)
Water							pCi/L				
	GS	192	73.8	γ, 0.316	N	(g)	(h)	0.5	2 – 3	Compton background from higher-energy γ-rays	DOE, MIW
Soil						grams	pCi/g				
	GS	192	73.8	γ, 0.316	N	50	(h)	0.5	2 – 3	Compton background from higher-energy γ-rays	DOE, MIW

Notes:

a. Method descriptions in Section 4.1
b. Units are MeV for decay particles, N/A for atom count methods (see Section 3.10)
c. Typical MDCs for DOE and MIW based on sample size and count time; see discussion in Section 3.3 and box on page 80
d. Time required to generate final data in laboratory (excluding data report generation or any QC validation)
e. Source as noted in Section 1.1
f. Medical/Industrial Waste is the most likely source (not discussed in this text).
g. Due to iridium's inertness and density, is unlikely to be found in water samples as a soluble component.
h. Because of its unusual nature as a contaminant, a routine MDC is not available. However, it may be detectable as low as 25 pCi/L (using filtration) or 25 pCi/g.

Alpha Spectrometry (AS), Accelerator Mass Spectrometry (AMS), Gas Flow Proportional Counting (GP), Gamma Spectrometry (GS), Inductively Coupled Plasma-Mass Spectrometric Analysis (ICP-MS), Kinetic Phosphoresence Analysis (KPA), Liquid Scintillation Counting (LSC), Thermal Ionization Mass Spectrometry (TIMS), Photon-Electron Rejecting Alpha Liquid Scintillation (PERALS®)

TABLE 9 — Lead

Matrix	Method (a)	Analyte	Half-Life (years)	Primary Energy of Detected Particle (b)	Chemical Separation (Y/N)	Sample Size	Typical MDC (c)	Total Analysis Time (days) (d)	Count Time (Hours)	Interfering Materials	Source (e)
Water						liters	pCi/L				
	GP	210	22.6	β, 0.017	Y	1	1.0	7	2 – 5	C-14	NORM
	GS (f)	210	22.6	γ, 0.0456	N	4	5	1	5	Sample self-attenuation; ^{210}Pb inherent in γ shielding	NORM
Soil						grams	pCi/g				
	GP	210	22.6	β, 0.017	Y	1	5	7	5 – 10	C-14	NORM
	GS (f)	210	22.6	γ, 0.0456	N	100	50	1	10	Sample self-attenuation; ^{210}Pb inherent in γ shielding	NORM

Notes: (All beta-particle energies are beta maximums)

a. Method descriptions in Section 4.1
b. Units are MeV for decay particles, N/A for atom count methods (see Section 3.10)
c. Typical MDCs for NORM based on sample size and count time; see discussion in Section 3.3 and box on page 80
d. Time required to generate final data in laboratory (excluding data report generation or any QC validation)
e. Source as noted in Section 1.1
f. Because of low gamma energy, extended range or low-energy detector (REGe or LEGe) is needed.

Alpha Spectrometry (AS), Accelerator Mass Spectrometry (AMS), Gas Flow Proportional Counting (GP), Gamma Spectrometry (GS), Inductively Coupled Plasma-Mass Spectrometric Analysis (ICP-MS), Low-Energy Germanium (LEGe), Kinetic Phosphorescence Analysis (KPA), Liquid Scintillation Counting (LSC), Reverse-Energy Germanium (REGe), Thermal Ionization Mass Spectrometry (TIMS), Photon-Electron Rejecting Alpha Liquid Scintillation (PERALS®)

TABLE 10 — Nickel

Matrix	Method (a)	Analyte	Half-Life (years)	Primary Energy of Detected Particle (b)	Chemical Separation (Y/N)	Sample Size	Typical MDC (c)	Total Analysis Time (days) (d)	Count Time (Hours)	Interfering Materials (h)	Source (e)
Water						liters	pCi/L				
	GS (g)	59	7.6 × 10^4	X-ray, 0.00748	Y	0.2	5	1 – 2	3	Co-58	NPP, DOE
	GP	63	100	β, 0.0669	Y	0.2	10	1 – 2	5		NPP, DOE
	LSC	63	100	β, 0.0669	Y	0.2	10	1 – 2	2		NPP, DOE
	ICP-MS	59	7.6 × 10^4	N/A	Y	0.02		1 – 2	0.5	Ni-58:H, Fe-58:H	NPP, DOE
Soil						grams	pCi/g				
	GS (g)	59	7.6 × 10^4	X-ray, 0.00748	Y	1	5	2 – 3	3	Co-58	NPP, DOE
	GP	63	100	β, 0.0669	Y	1	10	2 – 3	5		NPP, DOE
	LSC	63	100	β, 0.0669	Y	1	10	2 – 3	2		NPP, DOE
	AMS	59	7.6 × 10^4	N/A	N	0.001	1.25 × 10^{-3}	1	0.5	Ni-58:H, Fe-58:H	NPP, DOE

Notes: (All beta-particle energies are beta maximums)

a. Method descriptions in Section 4.1
b. Units are MeV for decay particles, N/A for atom count methods (see Section 3.10)
c. Typical MDCs for NPP and DOE based on sample size and count time; see discussion in Section 3.3 and box on page 80
d. Time required to generate final data in laboratory (excluding data report generation or any QC validation)
e. Source as noted in Section 1.1
f. Unit is pCi per mass of analyte
g. X-ray region
h. For ICP-MS and AMS, mass interference occurs from combinations of other high-abundance atoms in the mass spectrometer. An example is isobaric interference for Ni-59 from the atom combination of Ni-58 and H (both stable isotopes and present in high concentrations relative to the Ni-59).

Alpha Spectrometry (AS), Accelerator Mass Spectrometry (AMS), Gas Flow Proportional Counting (GP), Gamma Spectrometry (GS), Inductively Coupled Plasma-Mass Spectrometric Analysis (ICP-MS), Kinetic Phosphorescence Analysis (KPA), Liquid Scintillation Counting (LSC), Thermal Ionization Mass Spectrometry (TIMS), Photon-Electron Rejecting Alpha Liquid Scintillation (PERALS®)

TABLE 11 — Phosphorus

Matrix	Method (a)	Analyte	Half-Life (days)	Primary Energy of Detected Particle (b)	Chemical Separation (Y/N)	Sample Size	Typical MDC (c)	Total Analysis Time (days) (d)	Count Time (Hours)	Interfering Materials	Source (e)
Water						liters	pCi/L				
	LSC	32	14.3	β, 1.71	N (f)	0.01	500	1	4	P-33, Sr-89	DOE
	LSC (g)	32	14.3	β, 1.71	Y	20	1	3	5	P-33, Sr-89	DOE
Soil						grams	pCi/g				
	LSC	32	14.3	β, 1.71	Y	1	10	2	5	P-33, Sr-89	DOE

Notes: (All beta-particle energies are beta maximums)

a. Method descriptions in Section 4.1
b. Units are MeV for decay particles, N/A for atom count methods (see Section 3.10)
c. Typical MDCs for DOE based on sample size and count time; see discussion in Section 3.3 and box on page 80
d. Time required to generate final data in laboratory (excluding data report generation or any QC validation)
e. Source as noted in Section 1.1
f. Benitez-Nelson and Buesseler (1998)
g. “No chemical separation” MDC applies only when no other radionuclides are present.

Alpha Spectrometry (AS), Accelerator Mass Spectrometry (AMS), Gas Flow Proportional Counting (GP), Gamma Spectrometry (GS), Inductively Coupled Plasma-Mass Spectrometric Analysis (ICP-MS), Kinetic Phosphoresence Analysis (KPA), Liquid Scintillation Counting (LSC), Thermal Ionization Mass Spectrometry (TIMS), Photon-Electron Rejecting Alpha Liquid Scintillation (PERALS®)

TABLE 12 — Plutonium

Matrix	Method (a)	Analyte	Half-Life (years)	Primary Energy of Detected Particle (b)	Chemical Separation (Y/N)	Sample Size	Typical MDC (c, h)	Total Analysis Time (days) (d)	Count Time (Hours)	Interfering Materials (i)	Source (e)
Water						liters	pCi/L				
	AS	238	87.7	α, 5.499	Y	1	0.1	1 – 2 days	10 – 24	Am-241	NPP, DOE
	AS	239	2.41×10^4	α, 5.156	Y	1	0.1 (h)	1 – 2 days	10 – 24		NPP, DOE
	AS	240	6.56×10^3	α, 5.156	Y	1					NPP, DOE
	AS	238	87.7	α, 5.499	Y	1	70 (f)	1	1	Am-241	
	AS	239	2.41×10^4	α, 5.156	Y	1	70 (h,f)	1	1		
	AS	240	6.56×10^3	α, 5.156	Y	1					
	LSC	241	14.4	β, 0.021	Y	1	15	1 – 2	1		NPP, DOE
	LSC	241	14.4	β, 0.021	Y	1	3,200	1	1		
	ICP-MS	239	2.41×10^4	N/A	Y	1	10^{-4}	1 – 2	0.05	U-238:H	NPP, DOE
	ICP-MS	240	6.56×10^3	N/A	Y	1	0.1	1 – 2	0.05	Ra-226:N	NPP, DOE
Soil						grams	pCi/g				
	AS	238	87.7	α, 5.499	Y	1	0.1	2 – 3	10 – 24	Am-241	NPP, DOE
	AS	239	2.41×10^4	α, 5.156	Y	1	0.1 (h)	2 – 3	10 – 24		NPP, DOE
	AS	240	6.56×10^3	α, 5.168	Y	1					NPP, DOE
	AS	238	87.7	α, 5.499	Y	1	100	1	1	Am-241	
	AS	239	2.41×10^4	α, 5.156	Y	1	944 (h)	1	1		
	AS	240	6.56×10^3	α, 5.168	Y	1					
	LSC	241	14.4	β, 0.021	Y	1	15	2 – 3	1		NPP, DOE
	LSC	241	14.4	β, 0.021	Y	1	1,000	1	1		
	AMS	238	87.7	N/A	Y	N/A	N/A	1	0.05	Ra-226:C	NPP, DOE
	AMS	239	2.41×10^4	N/A	Y	0.001	2.7×10^{-5} (g)	1	0.05	U-238:H	NPP, DOE
	AMS	240	6.56×10^3	N/A	Y	0.001	2.7×10^{-5} (g)	1	0.05	Ra-226:N	NPP, DOE

Notes: (All beta-particle energies are beta maximums)

a. Method descriptions in Section 4.1

b. Units are MeV for decay particles, N/A for atom count methods (see Section 3.10)

c. Typical MDCs for NPP and DOE based on sample size and count time; see discussion in Section 3.3 and box on page 80. Soil and water values for Pu-238 are conservative estimates

d. Time required to generate final data in laboratory (excluding data report generation or any QC validation)

e. Source as noted in Section 1.1

f. MDC for Pu-239 Am-241 in water represents the sum of Am-241, Pu-238, and Pu-239/240

g. Value is the number of pCi detected in 0.001 g of sample

h. Pu-239 and Pu-240 α-particle energies are too close to be distinguished. The activity reported is the sum of the two isotopes.

i. For ICP-MS and AMS, mass interferences occur from combinations of other high-abundance atoms in the mass spectrometer. An example is isobaric interference for Pu-240 from the atom combination of Ra-226 (potentially abundant) and N-14 (stable isotope present in high concentrations relative to Pu-240)

TABLE 13 — Radium

Matrix	Method (a)	Analyte	Half-Life (years)	Primary Energy of Detected Particle (b)	Chemical Separation (Y/N)	Sample Size	Typical MDC (c, h)	Total Analysis Time (days) (d)	Count Time (Hours)	Interfering Materials (h)	Source (e)
Water						liters	pCi/L				
	GP-a (g)	226	1.62×10^3	α, 4.78	Y	1	0.1	5	5 – 8	Th-230, U-234	NORM
	AS	226	1.62×10^3	α, 4.78	Y	1	0.1	1	8	Th-230, U-234	NORM
	GP-β	228	5.76	β, (f)	Y	2	0.5	3	6 – 8	Sr-90	NORM
	GS	226	1.62×10^3	γ, 0.186	Y	4	1.4	1	4	Pa-234	NORM
	PERALS®	226	1.62×10^3	α, 4.78	Y	1	2	1	8	Th-230, U-234	NORM
	GP	226	1.62×10^3	α, 4.78	Y	0.5	0.5	7	3 – 5		NORM
Soil						grams	pCi/g				
	GP-a (g)	226	1.62×10^3	α, 4.78	Y	1	0.1	7	5 – 8	Th-230, U-234	NORM
	AS	226	1.62×10^3	α, 4.78	Y	10	1	1.5	8	Sr-90, Th-230, U-234	NORM
	GP-β	228	5.76	β, (f)	Y	1	0.02	5	6 – 8		NORM
	GS	226	1.62×10^3	γ, 0.186	N	200	1.4	1	10	Pa-234	NORM
	PERALS®	226	1.62×10^3	α, 4.78	Y	10	1	2	8	Th-230, U-234	NORM

Notes: (All beta-particle energies are beta maximums)
a. Method descriptions in Section 4.1
b. Units are MeV for decay particles, N/A for atom count methods (see Section 3.10)
c. Typical MDCs for NORM based on sample size and count time; see discussion in Section 3.3 and box on page 80
d. Time required to generate final data in laboratory (excluding data report generation or any QC validation)
e. Source as noted in Section 1.1
f. The progeny Ac-228 is actually counted. Its β-particle energy is 1.2 MeV.
g. Using radon + progeny ingrowth method with Lucas cell.
h. Non-radioactive barium, calcium, and strontium are significant chemical interferences in the analysis of any radium isotope because of their similar chemical reactivity.

Alpha Spectrometry (AS), Accelerator Mass Spectrometry (AMS), Gas Flow Proportional Counting (GP), Gamma Spectrometry (GS), Inductively Coupled Plasma-Mass Spectrometric Analysis (ICP-MS), Kinetic Phosphoresence Analysis (KPA), Liquid Scintillation Counting (LSC), Thermal Ionization Mass Spectrometry (TIMS), Photon-Electron Rejecting Alpha Liquid Scintillation (PERALS®)

TABLE 14 — Strontium

Matrix	Method (a)	Analyte	Half-Life	Primary Energy of Detected Particle (b)	Chemical Separation (Y/N)	Sample Size (g)	Typical MDC (c)	Total Analysis Time (days) (d)	Count Time (Hours) (f)	Interfering Materials	Source (ef)
Water						liters	pCi/L				
	LSC	89	50.5 d	β, 1.49	Y	1.00	2	7 – 18	3 – 17	Ca/Mg, Ba-140	NPP, DOE
	LSC	90	28.8 y	β, 0.546	Y	1.00	1	7 – 18	3 – 17	Ca/Mg, Ba-140	NPP, DOE
	LSC	90	28.8 y	β, 0.546	Y	1.00	4,300	2	5	Ca/Mg	
	GPC	89	50.5 d	β, 1.49	Y	1.00	1	7 – 18	3 – 17	Ca/Mg, Ba-140	NPP, DOE
	GPC	90	28.8 y	β, 0.546	Y	1.00	0.2	7 – 18	3 – 17	Ca/Mg, Ba-140	NPP, DOE
	GPC	90	28.8 y	β, 0.546	Y	1.00	4,300	2	5	Ca/Mg	
Soil						grams	pCi/g				
	LSC	89	50.5 d	β, 1.49	Y	2	0.5	7 – 18	3 – 17	Ca/Mg, Ba-140	NPP, DOE
	LSC	90	28.8 y	β, 0.546	Y	2	1	7 – 18	3 – 17	Ca/Mg, Ba-140	NPP, DOE
	LSC	90	28.8 y	β, 0.546	Y	1.00	306,000	2	5	Ca/Mg	
	GPC	89	50.5 d	β, 1.49	Y	2	0.5	7 – 18	3 – 17	Ca/Mg, Ba-140	NPP, DOE
	GPC	90	28.8 y	β, 0.546	Y	2	0.1	7 – 18	3 – 17	Ca/Mg, Ba-140	NPP, DOE
	GPC	90	28.8 y	β, 0.546	Y	1.00	306,000	2	5	Ca/Mg	

Notes: (All beta-particle energies are beta maximums)

a. Method descriptions in Section 4.1

b. Units are MeV for decay particles, N/A for atom count methods (see Section 3.10)

c. Typical MDCs for NPP and DOE based on sample size and count time; see discussion in Section 3.3 and box on page 80

d. Time required to generate final data in laboratory (excluding data report generation or any QC validation)

e. Source as noted in Section 1.1

f. Sr-89 would not be present from DOE samples, so the analysis times are shorter and a single count would be sufficient.

Alpha Spectrometry (AS), Accelerator Mass Spectrometry (AMS), Gas Flow Proportional Counting (GP), Gamma Spectrometry (GS), Inductively Coupled Plasma-Mass Spectrometric Analysis (ICP-MS), Kinetic Phosphorescence Analysis (KPA), Liquid Scintillation Counting (LSC), Thermal Ionization Mass Spectrometry (TIMS), Photon-Electron Rejecting Alpha Liquid Scintillation (PERALS®)

TABLE 15 — Sulfur

Matrix	Method (a)	Analyte	Half-Life (days)	Primary Energy of Detected Particle (b)	Chemical Separation (Y/N)	Sample Size	Typical MDC (c)	Total Analysis Time (days) (d)	Count Time (Hours)	Interfering Materials	Source (e)
Water						liters	pCi/L				
	LSC	35	87.2	β, 0.167	Y	1	1	2	5	C-14, P-33, Tc-99	DOE
	LSC	35	87.2	β, 0.167	N	1	10	2	5	C-14, P-33, Tc-99	DOE
Soil						grams	pCi/g				
	LSC	35	87.2	β, 0.167	Y	1	1	2	5	C-14, P-33, Tc-99	DOE
	LSC	35	87.2	β, 0.167	N	1	10	2	5	C-14, P-33, Tc-99	DOE

Notes: (All beta-particle energies are beta maximums)

a. Method descriptions in Section 4.1

b. Units are MeV for decay particles, N/A for atom count methods (see Section 3.10)

c. Typical MDCs for DOE based on sample size and count time; see discussion in Section 3.3 and box on page 80

d. Time required to generate final data in laboratory (excluding data report generation or any QC validation)

e. Source as noted in Section 1.1

Alpha Spectrometry (AS), Accelerator Mass Spectrometry (AMS), Gas Flow Proportional Counting (GP), Gamma Spectrometry (GS), Inductively Coupled Plasma-Mass Spectrometric Analysis (ICP-MS), Kinetic Phosphoresence Analysis (KPA), Liquid Scintillation Counting (LSC), Thermal Ionization Mass Spectrometry (TIMS), Photon-Electron Rejecting Alpha Liquid Scintillation (PERALS®)

TABLE 16 — Technetium

Matrix	Method (a)	Analyte	Half-Life (years)	Primary Energy of Detected Particle (b)	Chemical Separation (Y/N)	Sample Size	Typical MDC (c)	Total Analysis Time (days) (d)	Count Time (Hours)	Interfering Materials	Source (e)
Water						liters	pCi/L				
	LSC	99	2.135×10^5	β, 0.294	Y	0.25	15	2	5		NPP, DOE
	GP	99	2.135×10^5	β, 0.294	Y	0.25	15	2	5		NPP, DOE
	ICP-MS	99	2.135×10^5	N/A	Y	0.25	9×10^{-3}	2	0.05		NPP, DOE
Soil						grams	pCi/g				
	LSC	99	2.135×10^5	β, 0.294	Y	2	15	2	5		NPP, DOE
	GP	99	2.135×10^5	β, 0.294	Y	0.25	15	2	5		NPP, DOE
	ICP-MS	99	2.135×10^5	N/A	Y	20	0.02	2	0.05		NPP, DOE
	AMS	99	2.135×10^5	N/A	N	10	2×10^{-4}	1	0.05		NPP, DOE

Notes: (All beta-particle energies are beta maximums)

a. Method descriptions in Section 4.1

b. Units are MeV for decay particles, N/A for atom count methods (see Section 3.10)

c. Typical MDCs for NPP and DOE based on sample size and count time; see discussion in Section 3.3 and box on page 80

d. Time required to generate final data in laboratory (excluding data report generation or any QC validation)

e. Source as noted in Section 1.1

Alpha Spectrometry (AS), Accelerator Mass Spectrometry (AMS), Gas Flow Proportional Counting (GP), Gamma Spectrometry (GS), Inductively Coupled Plasma-Mass Spectrometric Analysis (ICP-MS), Kinetic Phosphoresence Analysis (KPA), Liquid Scintillation Counting (LSC), Thermal Ionization Mass Spectrometry (TIMS), Photon-Electron Rejecting Alpha Liquid Scintillation (PERALS®)

TABLE 17 — Thorium

Matrix	Method (a)	Analyte	Half-Life	Primary Energy of Detected Particle (b)	Chemical Separation (Y/N)	Sample Size	Typical MDC (c)	Total Analysis Time (days) (d)	Count Time (Hours)	Interfering Materials	Source (e)
Water						liters	pCi/L				
	AS	227	18.7 d	α, 6.04	Y	1	1	2	2		NORM, DOE
	AS	228	1.9 y	α, 5.42	Y	0.2	1	2	2		NORM, DOE
	AS	230	7.54×10^4 y	α, 4.69	Y	0.2	1	2	2		NORM, DOE
	AS	232	1.4×10^{10} y	α, 4.01	Y	0.2	1	2	2		NORM, DOE
	ICP-MS	232	1.4×10^{10} y	N/A	Y	10^{-3}	1	1	2	^{238}U, ^{235}U	NORM, DOE
	GS	228	1.9 y	γ, 0.084	N	4	15	1	6		NORM, DOE
	PERALS®	232	1.4×10^{10} y	α, 4.01	Y	0.25	0.1	2	24	^{238}U	NORM, DOE
Soil						grams	pCi/g				
	AS	227	18.7 d	α, 6.04	Y	2	0.6	3	2		NORM, DOE
	AS	228	1.9 y	α, 5.42	Y	2	0.6	3	2		NORM, DOE
	AS	230	7.54×10^4 y	α, 4.69	Y	2	0.6	3	2		NORM, DOE
	AS	232	1.4×10^{10} y	α, 4.01	Y	2	0.6	3	2		NORM, DOE
	ICP-MS	232	1.4×10^{10} y	N/A	Y	2.50×10^{-4}	19 pg (66 pCi)	3	2	^{238}U, ^{235}U	NORM, DOE
	GS	228	1.9 y	γ, 0.084	N	4	15	1	6		NORM, DOE
	PERALS®	232	1.4×10^{10} y	α, 4.01	Y	2	0.5	2	24	^{238}U	NORM, DOE

Notes:

a. Method descriptions in Section 4.1
b. Units are MeV for decay particles, N/A for atom count methods (see Section 3.10)
c. Typical MDCs for DOE and NORM based on sample size and count time; see discussion in Section 3.3 and box on page 80
d. Time required to generate final data in laboratory (excluding data report generation or any QC validation)
e. Source as noted in Section 1.1

Alpha Spectrometry (AS), Accelerator Mass Spectrometry (AMS), Gas Flow Proportional Counting (GP), Gamma Spectrometry (GS), Inductively Coupled Plasma-Mass Spectrometric Analysis (ICP-MS), Kinetic Phosphorescence Analysis (KPA), Liquid Scintillation Counting (LSC), Thermal Ionization Mass Spectrometry (TIMS), Photon-Electron Rejecting Alpha Liquid Scintillation (PERALS®)

TABLE 18 — Uranium

Matrix	Method (a)	Analyte	Half-Life (years)	Primary Energy of Detected Particle (b)	Chemical Separation (Y/N)	Sample Size	Typical MDC (c)	Total Analysis Time (days) (d)	Count Time (Hours)	Interfering Materials	Source (e)
Water						liters	pCi/L				
	AS	234	2.46×10^5	α, 4.776	Y	0.2	1	2	10		NORM, DOE
	AS	235	7.04×10^8	α, 4.395	Y	0.2	1	2	10		NORM, DOE
	AS	238	4.47×10^9	α, 4.197	Y	0.2	1	2	10		NORM, DOE
	KPA	Total	N/A	N/A	N	0.002	0.5 (0.34 ppb)	0.2	0.5	(g)	NORM, DOE
	PERALS®	238	4.47×10^9	α, 4.197	Y	0.5	2	2	12	Th-232	NORM, DOE
	PERALS®	234	2.46×10^5	α, 4.776	Y	0.5	3	2	12	Th-232	NORM, DOE
	ICP-MS	234	2.46×10^5	N/A	Y	0.1	$\sim 6 \times 10^{-5}$ ($\sim 10^{-15}$g)	1 – 2	0.05		NORM, DOE
	ICP-MS	235	7.04×10^8	N/A	Y	0.1	$\sim 2 \times 10^{-8}$ ($\sim 10^{-15}$g)	1 – 2	0.05		NORM, DOE
	ICP-MS	238	4.47×10^9	N/A	Y	0.1	$\sim 3 \times 10^{-9}$ ($\sim 10^{-15}$g)	1 – 2	0.05		NORM, DOE
	ICP-MS	234	2.46×10^5	N/A	N (h)	0.1	120 (0.02 µg/L)[h]	0.5	0.05		NORM, DOE
	ICP-MS	235	7.04×10^8	N/A	N (h)	0.1	0.04 (0.02 µg/L)[h]	0.5	0.05		NORM, DOE
	ICP-MS	238	4.47×10^9	N/A	N (h)	0.1	7×10^{-3} (0.02 µg/L)[h]	0.5	0.05		NORM, DOE
Soil						grams	pCi/g				
	AS	234	2.46×10^5	α, 4.776	Y	2	0.6	3	10		NORM, DOE
	AS	235	7.04×10^8	α, 4.395	Y	2	0.6	3	10		NORM, DOE
	AS	238	4.47×10^9	α, 4.197	Y	2	0.6	3	10		NORM, DOE
	AS	234	2.46×10^5	α, 4.776	Y	2	1,300	2	0.5		
	AS	235	7.04×10^8	α, 4.395	Y	2	1,300	2	0.5		
	AS	238	4.47×10^9	α, 4.197	Y	2	1,300	2	0.5		
	KPA	Total	N/A	N/A	Y	1	3.5×10^{-4} (1 ng/g)	1	0.5	(g)	NORM, DOE
	KPA	Total	N/A	N/A	Y	1	3,300 (9.65 mg/g)	0.2	0.5	(g)	
	PERALS®	238	4.47×10^9	α, 4.197	Y	5	1	2	15	Th-232	NORM, DOE
	PERALS®	234	2.46×10^5	α, 4.776	Y	5	2	2	15	Th-232	NORM, DOE
	ICP-MS	234	2.46×10^5	N/A	Y	10	3.1 (0.5 ng/g)[f]	1 – 2	0.05		NORM, DOE
	ICP-MS	235	7.04×10^8	N/A	Y	10	$1.1\text{x}10^{-3}$ (0.5 ng/g)[f]	1 – 2	0.05		NORM, DOE
	ICP-MS	238	4.47×10^9	N/A	Y	10	$1.7\text{x}10^{-4}$ (0.5 ng/g)[f]	1 – 2	0.05		NORM, DOE

Notes:

a. Method descriptions in Section 4.1

b. Units are MeV for decay particles, N/A for atom count methods (see Section 3.10)

c. Typical MDCs for DOE and NORM based on sample size and count time; see discussion in Section 3.3 and box on page 80

d. Time required to generate final data in laboratory (excluding data report generation or any QC validation)

e. Source as noted in Section 1.1

f. From ASTM Method C1345

g. Fluorescent materials

h. From ASTM Method D5673-03 and EPA 200.8. Requires sample preparation of the 100 mL sample. See references for details.

Alpha Spectrometry (AS), Accelerator Mass Spectrometry (AMS), Gas Flow Proportional Counting (GP), Gamma Spectrometry (GS), Inductively Coupled Plasma-Mass Spectrometric Analysis (ICP-MS), Kinetic Phosphoresence Analysis (KPA), Liquid Scintillation Counting (LSC), Thermal Ionization Mass Spectrometry (TIMS), Photon-Electron Rejecting Alpha Liquid Scintillation (PERALS®)

Appendix E: Nuclear Power Plant Decommissioning Sites

The decommissioning of commercial nuclear power facilities, and the required radionuclide analyses for that specific process, are regulated by the Nuclear Regulatory Commission. However, for completeness, this appendix provides an overview of issues associated with nuclear power facilities. The radionuclides found at these sites will be products of nuclear fission and nuclear activation. Table 12 identifies the most commonly encountered radionuclides at these sites.

Since the 1970s, 20 major commercial nuclear power plants (NPPs) throughout the country have shut down and are in various stages of decommissioning, including SAFSTOR. SAFSTOR is a decommissioning process in which the nuclear facility is placed and maintained in such a condition that the nuclear facility can be safely stored and subsequently decontaminated to levels that permit release for unrestricted use. These nuclear power stations use boiling water reactors (BWR), pressurized water reactors (PWR), or high-temperature gas-cooled reactors (HTGR). Table 11 lists the NPPs currently under some stage of decommissioning.

TABLE 11 — Decommissioning status for shut-down power reactors

Reactor	Type	Thermal Power	Location	Shutdown	Status	Fuel Onsite
Indian Point I	PWR	615 MW	Buchanan, NY	10/31/74	SAFSTOR	Yes
Dresden I	BWR	700 MW	Morris, IL	10/31/78	SAFSTOR	Yes
Fermi I	Fast Breeder	200 MW	Monroe Co., MI	9/22/72	SAFSTOR	No
GE VBWR	BWR	50 MW	Alameda Co., CA	12/9/63	SAFSTOR	No
Yankee Rowe	PWR	600 MW	Franklin Co., MA	10/1/91	DECON	Yes
CVTR	Pressure Tube, Heavy Water	65 MW	Parr, SC	1/67	License Terminated	No
Big Rock Point	BWR	67 MW	Charlevoix, MI	8/97	DECON	Yes
Pathfinder	Superheat BWR	190 MW	Sioux Falls, SD	9/16/67	DECON NRC Part 30	No
Humboldt Bay 3	BWR	200 MW	Eureka, CA	7/02/76	SAFSTOR	Yes
Peach Bottom I	HTGR	115 MW	York Co., PA	10/31/74	SAFSTOR	No
San Onofre I	PWR	1347 MW	San Clemente, CA	11/30/92	DECON	Yes
Haddam Neck	PWR	1825 MW	Haddam Neck, CT	7/22/96	DECON	Yes
Fort St. Vrain	HTGR	842 MW	Platteville, CO	8/18/89	License Terminated	Yes
Millstone I	BWR	2011 MW	Waterford, CT	11/04/95	DECON	Yes
Zion I	PWR	3250 MW	Zion, IL	2/98	SAFSTOR	Yes
Zion 2	PWR	3250 MW	Zion, IL	2/98	SAFSTOR	Yes
Maine Yankee	PWR	2772 MW	Bath, ME	12/96	DECON	Yes
Rancho Seco	PWR	2772 MW	Sacramento, CA	6/7/89	DECON	Yes
Three Mile Island 2	PWR	2772 MW	Middletown, PA	3/28/79	SAFSTOR*	No
Saxton	PWR	28 MW	Saxton, PA	5/72	DECON	No
Shoreham	BWR	2436 MW	Suffolk Co., NY	6/28/89	License Terminated	No
Trojan	PWR	3411 MW	Portland, OR	11/9/92	DECON	Yes
LaCrosse	BWR	165 MW	LaCrosse, WI	4/30/87	SAFSTOR	Yes

* Post-defueling monitored storage (PDMS).

Since 1989, most of the NPPs undergoing active decommissioning (rather than SAFSTOR) are in the northeast, including Shoreham in New York, Yankee Rowe in Massachusetts, Maine Yankee in Maine, and Hadden Neck and Millstone I in Connecticut. The Indian Point I NPP in New York is in SAFSTOR, and Shoreham NPP in New York has been decommissioned and its license terminated.

Most NPPs undergoing decommissioning will follow the guidance in the Multi-Agency Radiation Survey and Site Investigation Manual (MARSSIM, 2000) and perform a site characterization study. Site characterization combines the information gathered during a historical site assessment (HSA) and radiation surveys or sampling of the various affected and unaffected areas of the site. The purpose of a HSA is to identify:

- The radionuclides generated or used at the site during its operation and any potential residual contamination by these radionuclides;
- Potentially contaminated areas; and
- Potentially contaminated media, including buildings, surface and ground water, surface and subsurface soil/media, and sediment.

The decommissioning process involves the dismantling and disposal of the NPP by component and structure, the transfer of the spent fuel to interim storage facilities, the cleanup of residual surface and subsurface contamination onsite and cleanup of offsite contamination from previous operations, and the decommissioning process.

The nuclides that may be found at nuclear power stations undergoing decommissioning include the fission and activation products generated during the operation of the plant. The nuclides found depend on the type of reactor, fuel components, and the time interval to initiate the decommissioning process after the plant is shut down. For example, the nuclides and their activity levels generated in a HTGR are very different than those generated by a BWR or PWR. In addition, certain radionuclides are more prevalent in PWR than BWR, and even within a reactor type, certain nuclides may be characteristic to specific fuel components, e.g., ^{108m}Ag and ^{110m}Ag for a PWR.

In most cases, NPP personnel will have knowledge of the nuclides present onsite and in the environment as a result of power generation operations. Usually a detailed nuclide characterization of the radioactivity onsite is determined as a result of requirements to meet 10 CFR 61 for waste disposal of materials from various waste streams in a NPP and 10 CFR 50 for effluent monitoring requirements. Regulations codified at 10 CFR 61 require the quantification of the most active radionuclides as well as the hard-to-detect (difficult-to-measure), long-lived, pure alpha and beta nuclides for each identified waste stream, e.g., primary coolant, primary cleanup components such as filters and resins, crud, dry active waste, and metal components. The former category includes the gamma-ray emitting nuclides having a half-life greater than 0.1 years. Table 12 provides a listing of the nuclides requiring quantification, their physical characteristics, the required detection limits to be met during analyses and the typical techniques for detection and chemical yield determination. For these "Part 61" measurements, scaling factors (based on the activity ratios) are calculated between the easier to detect gamma emitting nuclides and the hard-to-detect nuclides.

During operations and maintenance of a nuclear plant, there is a potential for the dispersion of radioactive materials onsite, and in some cases, for subsurface dispersion from leaking tanks or piping or spills. In addition, normal liquid effluent releases can result in the buildup of certain longer-lived radionuclides in the sediment of rivers, reservoirs or impoundments. During the decommissioning process involving the dismantlement and transfer of highly radioactive structures (component of the reactor, reactor vessel, pressurizers, primary coolant piping and valves, spent fuel pool and fuel transfer areas, and structural support materials), there may be a possibility that radioactive materials may spread to other areas of the site or to the offsite environs.

TABLE 12 — Important parameters associated with NPP analyses

Nuclide	Half-life (year)	Radiation Emitted (keV)*	Detection Technique†	MDC (nCi/g)	Chemical Yield Determination
γ Emitters	> 0.1	γ(100 - 2000)	Ge detector - γ spectrometry	^{137}Cs: 10, others: 7,000	No chemical separation — direct measurement
^{3}H	12.3	β (18.6)	LS	400	No chemical separation— direct measurement
^{14}C	5,730	β (156)	LS	80	Gravimetric
^{55}Fe‡	2.7	X-Ray (5.89)	Low-energy Ge/Si, LS	7,000	ICP, AA
^{59}Ni	75,000	X-Ray (6.92)	Low-energy Ge/Si, LS	2,200	ICP, AA
^{63}Ni	100	β (65.9)	LS	35	ICP, AA
^{90}Sr	28.6	β (546)	GP, Cerenkov - LS	0.4	Gravimetric, ^{85}Sr
^{94}Nb‡	20,300	β (471), γ(703, 871)	Ge detector - γ spectrometry	2	ICP
^{99}Tc	2.13×10^{5}	β (294)	GP, LS	30	^{99m}Tc, Re (ICP-MS)
^{129}I	1.57×10^{7}	β (152), γ(39.6)	Low-energy Ge/Si, LS, GP	0.8	Gravimetric
^{237}Np‡	2.14×10^{6}	α (4771, 4788), γ(86.5, 29.4)	α spectrometry	1	^{239}Np
^{238}Pu	87.8	α (5436, 5499)	α spectrometry	1	^{236}Pu or ^{242}Pu
^{239}Pu	24,100	α (5105, 5143, 5155)	α spectrometry	1	^{236}Pu or ^{242}Pu
^{240}Pu	6,570	α (5123, 5168)	α spectrometry	1	^{236}Pu or ^{242}Pu
^{241}Pu	14.4	β (20.8)	LS	35	^{236}Pu or ^{242}Pu
^{242}Pu	3.76×10^{5}	α (4856, 4901)	α spectrometry	1	^{236}Pu
^{241}Am	432	α (5443, 5485), γ(59)	α spectrometry, γ spectrometry	1	^{243}Am
^{243}Am	7,380	α (5234, 5279), γ(74.7)	α spectrometry, γ spectrometry	1	—
^{242}Cm‡	0.446	α (6069, 6113)	α spectrometry	1	^{243}Am
^{243}Cm‡	28.5	α (5742, 5784), γ(228, 278)	α spectrometry, γ spectrometry	1	^{243}Am
^{244}Cm‡	18.1	α (5763, 5805)	α spectrometry	1	^{243}Am

* For beta emitters, column refers to maximum energy.

† LS – liquid scintillation, Ge – germanium semiconductor, Si – silicon semiconductor, GP – gas proportional counting, ICP – inductively coupled plasma analysis, ICP-MS – inductively coupled plasma-mass spectrometry, AA – atomic absorption

‡These radionuclides are included in this table for completeness, but are not discussed in this document.

The information gained from the 10 CFR 61 analyses (scaling factors) may be used to estimate the levels of the hard-to-detect radionuclides in contaminated materials, subsurface soils or ground water. If hard-to-detect radionuclides are suspected for a given waste discharge or contamination process, the easier-to-detect gamma-emitting nuclides are quantified, and then the hard-to-detect nuclides are estimated from applying the scaling factors or analyzed at an offsite contract laboratory that can provide the required detection capability.

The primary gamma-ray emitting nuclides found at most NPPs undergoing decommissioning include ^{60}Co, ^{134}Cs, ^{137}Cs, ^{152}Eu, ^{154}Eu, and ^{155}Eu. If decommissioning is initiated within a few years after plant shutdown, ^{54}Mn, ^{65}Zn, and ^{57}Co may be present in sufficient quantities to be detected by gamma-ray spectrometry. NRC (1978 and 1984) list the radionuclides existing in concrete, rebar, and surface contamination.