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High Resolution Gamma-Ray Spectrometry Analyses For Normal Operations and Radiological Incident Response

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

This report was prepared for the National Analytical 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 EP-W-13-016, Task Order 014, managed by Daniel Askren. Mention of trade names or specific applications does not imply endorsement or acceptance by EPA.

PREFACE

This document is one of several initiatives by EPA's Office of Radiation and Indoor Air (ORIA) designed to provide guidance to radioanalytical laboratories that will support EPA's response and recovery actions following a radiological or nuclear incident. This guide examines the analysis of samples by gamma-ray spectrometry during normal operations and following a radiological incident. The guidance provided in this document for the screening and analysis of samples should assist those federal, state, and commercial radioanalytical laboratories that will be challenged with a large number of such samples when responding to a radiological or nuclear incident. This document is applicable to different types of events; a radiological transportation incident, a radiological dispersal device (RDD or "dirty bomb"), a release from an emergency condition at a nuclear power plant, or the detonation of an improvised nuclear device (IND), other potential radiological releases as well as normal laboratory operations. These samples will be contaminated with varying levels of radionuclides and will represent matrices of varied composition. Advance planning by national and regional response teams, as well as by radiological laboratories, will be critical to ensure uninterrupted throughput of large numbers of radioactive samples and the rapid turnaround and reporting of results that meet required data quality objectives associated with the protection of human health and the environment. EPA's responsibilities, as outlined in the *National Response Framework, Nuclear/Radiological Incident Annex*, include response and recovery actions to detect and identify radioactive substances and to coordinate federal radiological monitoring and assessment activities.

Detailed guidance on recommended radioanalytical practices can be found in the *Multi-Agency Radiological Laboratory Analytical Protocols Manual* (MARLAP), which provides detailed radioanalytical guidance for project planners, managers, and radioanalytical personnel based on project-specific requirements (www.epa.gov/radiation/marlap/links.html). Familiarity with Chapters 2, 3, 14, 15 and 18-20 of MARLAP will be of significant benefit to users of this guide. This document is one in a series designed to present radioanalytical laboratory personnel, Incident Commanders (and their designees), and other field response personnel with key laboratory operational considerations and likely radioanalytical requirements, decision paths, and default data quality and measurement quality objectives for analysis of samples taken after a radiological or nuclear incident.

Documents currently completed include:

- *Radiological Laboratory Sample Analysis Guide for Incidents of National Significance – Radionuclides in Water* (EPA 402-R-07-007, January 2008)
- *Radiological Laboratory Sample Analysis Guide for Incidents of National Significance – Radionuclides in Air* (EPA 402-R-09-007, June 2009)
- *Radiological Laboratory Sample Screening Analysis Guide for Incidents of National Significance* (EPA 402-R-09-008, June 2009)
- *Method Validation Guide for Qualifying Methods Used by Radiological Laboratories Participating in Incident Response Activities* (EPA 402-R-09-006, June 2009)
- *Guide for Laboratories – Identification, Preparation, and Implementation of Core Operations for Radiological or Nuclear Incident Response* (EPA 402-R-10-002, June 2010)

- *A Performance-Based Approach to the Use of Swipe Samples in Response to a Radiological or Nuclear Incident* (EPA 600-R-11-122, October 2011)
- *Guide for Radiological Laboratories for the Control of Radioactive Contamination and Radiation Exposure* (EPA 402-R-12-005, August 2012)
- *Radiological Laboratory Sample Analysis Guide for Incident Response – Radionuclides in Soil* (EPA 402-R-12-006, September 2012)
- *Uses of Field and Laboratory Measurements During a Radiological or Nuclear Incident* (EPA 402-R-12-007, August 2012)

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- Martin Wright of Diablo Canyon Nuclear Power Plant
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Dedication

This guide is dedicated to the memory of our friend and colleague, Dr. David McCurdy. Dave worked as a consultant for EMS for over 23 years, beginning with the Multi-Agency Radiological Laboratory Analytical Protocols (MARLAP) manual in 1994. Dave served as EMS's QAPP Primary Investigator, instructed courses on topics such as MARLAP and basic radiochemistry, assisted in the method validation process, and was a key contributor to the publication of incident response guidance. In his spare time, Dave enjoyed fly-fishing, tennis, and traveling. He left many friends throughout EPA and the radioanalytical community, and he will be greatly missed.

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ACRONYMS AND ABBREVIATIONS

(*Excluding chemical symbols and formulas*)

α	alpha particle
α	probability of Type I decision error
A	mass number
ADC	analog-to-digital converter
ASTM	American Society for Testing and Materials
β	beta particle
β	probability of Type II decision error
β^-	negatron or beta-minus particle
β^+	positron or beta-plus particle
Bq	becquerel (1 dps)
BNL	Brookhaven National Laboratory
CFR	Code of Federal Regulations
Ci	curie
cm	centimeter
cpm	counts per minute
d	day
DDC	decay during counting
DDEP	Decay Data Evaluation Project
DOE	United States Department of Energy
DP	decay product(s)
dpm	disintegration per minute
dps	disintegration per second
DRL	derived response levels
DRP	discrete radioactive particle
ε	electron capture
$E_{\beta\mathrm{max}}$	maximum energy of the beta-particle emission
ERLN	Environmental Response Laboratory Network
EPA	United States Environmental Protection Agency
FRMAC	Federal Radiological Monitoring and Assessment Center
FWHM	full width half maximum
γ	gamma radiation
g	gram
Ge	germanium semiconductor
Gy	gray
h	hour
HPGe	high-purity germanium [detector]
IC	incident commander
IC	internal conversion
ICLN	Integrated Consortium of Laboratory Networks
IND	improvised nuclear device (i.e., a nuclear bomb)
in	inch
IT	isomeric transition
kg	kilogram (10^3 gram)
keV	kiloelectronvolts (10^3 electronvolts)

L ....liter
LNHB…………Laboratoire Nationale de Henri Becquerel
MARLAP..........*Multi-Agency Radiological Laboratory Analytical Protocols Manual*
MCA ....multichannel Analyzer
mCi...................millicurie (10^{-3} Ci)
MeV ....megaelectronvolts (10^{6} eV)
mg ....milligram (10^{-3} g)
mL ....milliliter (10^{-3} L)
mrem ....millirem (10^{-3} rem)
µCi....................microcurie (10^{-6} curie)
µg ....microgram (10^{-6} g)
MDA ....minimum detectable activity
MDC ....minimum detectable concentration
min ....minute
MQO ....measurement quality objective
NAREL ....EPA National Analytical Radiation Environmental Laboratory
NNDC ....National Nuclear Data Center, Brookhaven National Laboratory
NORM..............naturally-occurring radioactive materials
NUDAT............NNDC NUDAT database
ORIA................EPA Office of Radiation and Indoor Air
PAG..................protective action guide
pCi....................picocurie (10^{-12} Ci)
PT……………..proficiency test (sample)
QA....................quality assurance
QC ....quality control
rad ....radiation absorbed dose
RCS ....reactor coolant system
RDD ....radiological dispersal device (i.e., a dirty bomb)
RFA..................responsible federal agency
rem ....roentgen equivalent: man
s ....second
SI ....International System of Units
SOP ....standard operating procedure
STS……………sample test source
Sv ....Sievert
τ ....time frame
TCS……………true coincidence summing
TRU..................transuranic elements
WCS…………..working calibration standard
y………….……year

GLOSSARY

Excellent glossaries of radiological and radiochemical terms including those for gamma spectrometry can be found in ASTM D7902-14, “Standard Terminology for Radiochemical Analyses”, and also in the *Multi-Agency Radiological Laboratory Analytical Protocols Manual* (MARLAP). The terms used here are in the context of those references.

RADIOMETRIC UNIT CONVERSIONS

To Convert	To	Multiply by	To Convert	To	Multiply by
years (y)	seconds (s)	3.16×10^{7}	s	y	3.17×10^{-8}
	minutes (min)	5.26×10^{5}	min		1.90×10^{-6}
	hours (h)	8.77×10^{3}	h		1.14×10^{-4}
	days (d)	3.65×10^{2}	d		2.74×10^{-3}
disintegrations per second (dps)	becquerels (Bq)	1	Bq	dps	1
Bq	picocuries (pCi)	27.0	pCi	Bq	3.70×10^{-2}
Bq/kg	pCi/g	2.70×10^{-2}	pCi/g	Bq/kg	37.0
Bq/m^3	pCi/L	2.70×10^{-2}	pCi/L	Bq/m^3	37.0
Bq/m^3	Bq/L	10^{-3}	Bq/L	Bq/m^3	10^{3}
microcuries per milliliter (µCi/mL)	pCi/L	10^{9}	pCi/L	µCi/mL	10^{-9}
disintegrations per minute (dpm)	µCi	4.50×10^{-7}	pCi	dpm	2.22
	pCi	4.50×10^{-1}	µCi		2.22×10^{6}
cubic feet (ft^3)	cubic meters (m^3)	2.83×10^{-2}	m^3	ft^3	35.3
gallons (gal)	liters (L)	3.79	L	gal	0.264
gray (Gy)	Rad	10^{2}	rad	Gy	10^{-2}
roentgen equivalent man (rem)	sievert (Sv)	10^{-2}	Sv	rem	10^{2}

NOTE: Traditional units are used throughout this document instead of International System of Units (SI) units. PAGs and their derived concentrations appear in official documents in the traditional units and are in common usage. Conversion to SI units will be aided by the unit conversions in this table.

I. BACKGROUND

Many of the country's radiological laboratories have not had the experience of analyzing environmental samples contaminated with levels of radioactivity up to one thousand times environmental levels and above. Even for those laboratories that have had experience with high activity concentration samples, fresh fission products have rarely been seen in environmental samples for the past 40 years[1]. The potential threat of an improvised nuclear device or a nuclear facility accident where fresh fission products are released requires that our nation have both the capability and capacity to analyze these specific types of radionuclides. Most of the fission products that would result from either type of event are gamma-ray emitters; this makes gamma-ray spectrometry a prime analytical tool for environmental analysis.

Historically, proficiency test (PT) samples have contained multiple radionuclides. With few exceptions[2], these have tended to be long-lived, many of which have not been fresh fission products (i.e., short-lived). The same radionuclides were repeatedly used in the PT samples, and most of the radionuclides used did not exhibit parent-progeny radiochemical equilibria. Thus, experience identifying and quantifying short-lived fission products and parent-progeny equilibrium radionuclides was lacking.

ORIA sponsored a contract to prepare four rounds of PT samples with fresh, short-lived fission products to address this specific issue. The PT samples were prepared by irradiating natural uranium, dissolving it and preparing aqueous samples containing elevated concentrations of radionuclides with half-lives of ~2 days or longer. These samples were analyzed several times by a reference laboratory and then sent to radiochemistry laboratories willing to participate in that project.

The first two rounds of samples were analyzed only by gamma-ray spectrometry by 11 to 30 participating laboratories. The results were tabulated and reports provided individually to laboratories on their performance as well as the group performance (with identities of other laboratories being maintained as confidential). The results were surprising as there was an overwhelming lack of experience with this type of sample and the use of the gamma-ray spectrometry systems used to analyze such a sample. Additionally, laboratories had trouble adhering to the analytical requirements and reporting criteria requested by EPA. Afterward, the criteria and instructions for analysis were refined to include more specific directions on analysis and reporting requirements. These can be found in Attachment I.

Two additional rounds of PT samples were prepared and distributed to 40 laboratories. There was an improvement in the analytical results that were reported and the reporting protocols that were followed in these next two events. However, there remained some concerns about how the laboratories were validating the results of their analyses and whether or not there was sufficient training for laboratory staff in the theory of gamma spectrometry and the operation of the gamma spectrometry systems and software.

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[1] The obvious exception is for those samples taken during the Chernobyl and Fukushima events. However, in both cases the types and activity concentrations of the fission products that were determined were far reduced due to the long atmospheric transport times of the radionuclides.

[2] For example, ^{131}I in water and milk.

Under a separate contract, site-specific training was provided to twelve state radiochemistry laboratories. One of the topics for onsite training was gamma spectrometry theory and practice. Some of the laboratories had also participated in the mixed fission product PT sample programs described above. While some of them provided very good results on the PT program, it was evident that their theoretical background in gamma spectrometry and software operation was limited. An example of the limited theoretical background was that laboratories relied too strongly on software analysis even though the reported results were improbable. Although software can be adapted to analyze a spectrum for different types of samples and radionuclides, many users did not understand the capabilities and limitations of the software, and how critical their role was in the configuration of the software to obtain accurate and reliable results.

Rapid measurements of activities that are precise and of known and reliable quality (e.g., accurate identification of radionuclides) are essential in both normal and emergency response situations. Radionuclides that are misidentified or activities that are inaccurate may lead to inappropriate actions on the part of the client. Thus, training in data review, as well as interpretation of spectral results, is essential. This guide was developed to be a tool to assist in training current and new gamma-ray spectrometrists.

A. Structure of the Document

Gamma-ray spectrometry analysis has progressed significantly since single-channel analysis was used in the 1950s and early 1960s. The energy resolution and efficiency of detection systems have improved since that era. Sophisticated software has been developed that increases the speed with which these analyses can be performed.

Prior to the advent of sophisticated software, practitioners gained more experience in assessing the identities of radionuclides from the direct review of the gamma-ray spectrum, understanding how radiochemical relationships affect activity calculations, and the determination of activity through hand calculations. A further complicating factor for current practitioners is that they likely have never seen samples that contain high activity (one thousand or more times background detection limits) or spectra that contain fresh fission products or a diversity of activation products (ones that would potentially be used in an RDD). This also makes it difficult for today's practitioners to assess how the radioactive decay laws are applied in the logic, algorithms, and calculations used in the internal software programs for the gamma-ray spectrometry system. Finally, in spite of the improved capabilities and sophistication of modern software, no standard commercially available gamma spectrometry analysis software has the capabilities to properly account for all parent-decay product activity relationships.

The purpose of this document is to provide guidance to laboratories performing gamma-ray spectrometric analyses of samples following a radiological or nuclear incident. Specific examples of analyses where environmental and process samples containing fresh fission products or other radionuclide combinations are addressed in this document in Attachment II. The following topics are described in general theoretical terms and some of each topic can be found in the examples:

- Processing gamma-ray spectra for identifying radionuclides.
- Radionuclide identification: gamma-ray energies and photons.
    - Radioactive decay modes.
    - Gamma-ray interactions with the detector.
    - Potential threat radionuclides.
    - Effects of high activity concentrations on interferences and identification.
        - Low abundance gamma rays of high activity radionuclides which are not listed in the libraries.
        - Gamma-ray interferences not anticipated.
        - Limited sensitivity due to high background.
        - Single-escape, double-escape and multiple-sum peaks.
        - Dead time corrections/adjustments due to high sample activity.
- Decay correction and count time.
    - Ensuring correct half-life.
- Decay correction and radiochemical equilibrium.
    - Parent-progeny equilibrium not established.
    - Parent-progeny equilibrium disturbed by chemical effects.
    - Proper use of software algorithms for decay and ingrowth correction.
    - Activity correction for cases where equilibrium has not yet been established (manual).
- Software.
    - Proper configuration for sample/matrix type, and geometry.
    - Validation tests used during analysis (peak identification, radionuclide association with a gamma ray, etc.).
    - Ensuring correct abundance.
    - Radionuclides are appropriate for the type of sample or matrix.
    - Activity (quantification) and detection equations.
    - Uncertainty.
- Selecting Detectors.
- Sample Preparation.
- Selecting Geometries, Counting Containers, Detection Equations, Count Intervals and Uncertainty Equations.
- Detector calibration and non-routine counting geometries.
- Correcting efficiencies for matrix effects.
- Establishing Sample Matrix/Specific Libraries in the Software.
- Gamma-ray spectrometry report review processes.
- Data validation and reporting protocols.
- Examples of radioanalytical results.

The information provided herein is a starting point for those performing gamma-ray spectrometric analyses. The document should be used in conjunction with analysis of actual samples containing activity levels that range from low-level to those which are much higher than normal, and where less commonly encountered short-lived radionuclides are present. Analyses performed in this manner will allow analysts to experience the types of problems that will be encountered during analysis of radiological event samples and resolved by using the guidance provided in this document.

B. Goals

This guide presents a generic approach to gamma-ray spectrometry. It describes the effects that gamma rays create in high-purity germanium (HPGe) detectors and in other materials and the general set-up and maintenance of HPGe systems and software. It also addresses various aspects of samples that may be encountered (radionuclide mixtures and matrix) and provides guidance that allows the user to review the results of measurements to ensure that the results will satisfy applicable measurement quality objectives (MQOs).

C. Objectives

The objectives of this document are as follows:
1. Describe the basic theoretical principles of gamma-ray spectrometry.
2. Show how the interactions of gamma rays with the HPGe detector can yield artifacts that cannot be used to quantify radionuclides
3. Explain the radioactive equilibria and demonstrate how to calculate radionuclide concentrations when these equilibria are present.
4. Provide examples of problems that can be encountered when analyzing specific matrices
5. Provide descriptions of the different software functions and how they are used in analyzing the gamma-ray spectrum.
6. Provide examples of analyses that were incorrectly performed by software based on preselected functions that were inappropriate for the type of sample analyzed, and how these problems can be avoided.
7. Identify the different types of detection equations and how they differ in their determination of detection.

II. PROCESSING SPECTRA FOR IDENTIFYING AND QUANTIFYING GAMMA-RAY EMITTING RADIONUCLIDES

A gamma-ray spectrum is generated when gamma rays interact with a detector. Electronic pulses are produced with amplitude proportional to the energy these gamma rays deposited in the detector. The pulses are shaped, amplified, and stored by signal processing electronics that normally includes an amplifier, an analog-to-digital converter (ADC), and a multi-channel analyzer (MCA) that stores the pulses in digital memory according to energy. The resulting data is displayed graphically as a histogram or spectrum showing the number of observations (counts) as a function of gamma-ray energy. An example of a spectrum of ^{60}Co is shown in Figure 8. The characteristics of a gamma-ray spectrum are discussed below.

Modern gamma-ray spectrometry systems include a high-resolution high purity germanium (HPGe) detector plus electronics interfaced to a computer system with software to process spectra and calculate the concentration of radionuclides in samples. The complexity of gamma-ray spectra that may be encountered in emergency response scenarios precludes the processing of spectra manually. Many software packages provide the tools for setup and calibration of the systems for processing spectra. Two major suppliers in the United States[3] provide sophisticated software for processing spectra. The individual components of the software necessary for analyzing samples will be discussed in Section F. The reader is also referred to an excellent discussion of "Computer Analysis of Gamma-Ray Spectra" in Chapter 9, Reference 22.

Figure 1 (from Reference 21) shows a generic flow process for spectral analysis of a sample applicable to most software capable of complete analyses of spectra. In practice, software packages may implement unique approaches that optimize performance to address different analytical challenges. Thus, one approach may be more appropriate for analyzing low-activity samples with a limited set of radionuclides (e.g., naturally-occurring radionuclides), whereas a different approach may be optimal for analyzing high-activity samples containing many radionuclides, or for samples that may contain radionuclides that may be present in more complex decay relationships.

The laboratory's Quality Manual for Radiochemistry should include any specific objectives of the lab, but more importantly, it should identify the source documents from which all parameters in the library originate. This kind of document is vital for succession planning, training of new personnel, and the important standardization of parameters like energy lines, abundances, and half-lives. For example, this document may state that all parameters of this sort are obtained from the NUDAT database.

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[3] Canberra Industries, Inc. and AMETEK ORTEC

NOTE

A number of nuclear databases are commonly used by gamma spectrometrists. Some of these, such as Kocher (*Radioactive Decay Data Tables*, D.C. Kocher, DOE/TIC-11026, 1981) and several libraries supplied by instrument manufacturers, are outdated and do not reflect the currently, best-available nuclear data. The Decay Data Evaluation Project (DDEP) is an international collaboration of radiological laboratories. DDEP data files can be accessed at Henri Becquerel Laboratories (LNHB, http://www.nucleide.org/DDEP_WG/DDEPdata.htm). The data in DDEP is quite reliable as it has undergone extensive validation. It also contains extensive details regarding nuclear constants.

This guide, however, recommends using the Decay Radiation Database at the National Nuclear Data Center (NNDC) website, commonly referred to as NUDAT. Although this online database is routinely updated and contains up-to-date nuclear data, it may not be as carefully reviewed as DDEP data. However, it contains a much more comprehensive collection of nuclear data that is much more easily accessible using a powerful query interface. The data are also presented in a manner that is more compatible with the preparation of gamma spectrometry libraries. The more comprehensive collection of data is also invaluable when searching for unidentified photopeaks in gamma spectra.

While we recommend routinely using NNDC/NUDAT, we also recommend using the more reliable DDEP data to validate the abundant library lines that drive the quantification of gamma emitters (the top 3-4 for a nuclide). Similarly, we recommend relying on DDEP data whenever there is any concern over the correctness of nuclear data found elsewhere.

This effort will prevent a common failure related to lab performance degradation after key people leave the lab through retirement, etc. and also improve general communication should more than one person be involved in maintenance/review of the libraries.

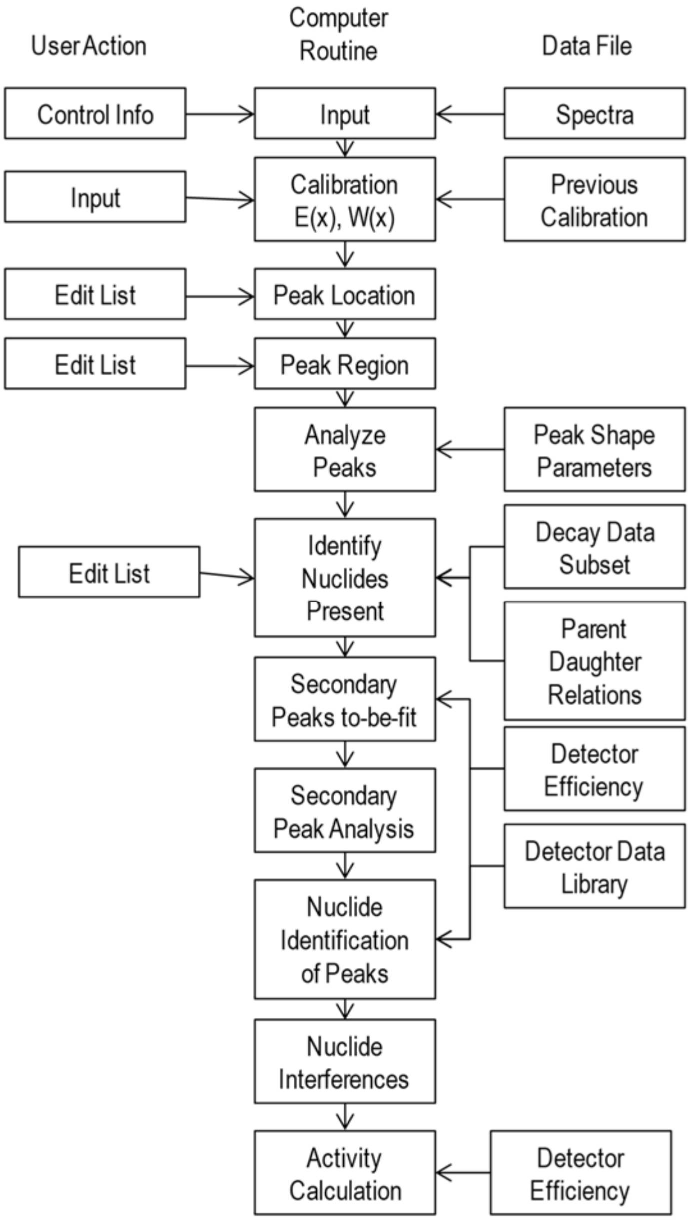

Figure 1. Software Process Flow for Gamma-Ray Spectrum Analysis

The functionality of the various computer routines identified in the above table is discussed in detail in Section F, Software Preset Functions.

III. RADIOACTIVE DECAY MODES

Two decay modes that can precede gamma-ray emission are alpha (α) and beta (β) decay. Beta decay is further subdivided into negatron (β^-), positron (β^+) and electron capture (ε) decay.

Decay only by the emission of a gamma ray (without beta or alpha particle emission) is referred to as isomeric transition[4] (IT).

Most radioactive decay by an alpha particle or beta particle emission does not result in the release of sufficient energy for the decay product to be left at its lowest possible energy (ground) state. The remaining energy to reduce the energy state of the decay product to the ground state is normally released in the form of a gamma ray. Gamma rays are released from the excited state of the decay products at discrete energies.

Radioactive decay may also include emission of characteristic X-rays. X-rays are the result of an electron in a bound shell being expelled and the subsequent rearrangement that occurs when higher energy electrons fall to vacant, lower energy states. The emitted characteristic X-ray will have energy equal to the difference between the two energy states. X-ray emission will always follow electron capture decay and may follow β^-, β^+, alpha, internal conversion (IC) and IT decay processes. Internal conversion is a result of a nucleus in an excited state transferring all its energy directly to a bound electron (highest probability is a K-shell electron), and decreasing the probability of gamma-ray emission.

Figure 2, from the Brookhaven National Laboratory NuDat database[5], shows the entire range of known radioactive and stable nuclides. A small section of the chart centered at about ^{140}La is expanded to show some of the detail from the NuDat website diagram. The black boxes represent stable nuclides[6]. All other colors represent nuclides that are radioactive. A diagonal drawn through the average trend of the black boxes is referred to as the "line of stability". All radionuclides to the right of the line of stability have a neutron excess, while those to the left of the line have a neutron deficiency. Those radionuclides to the right will decay mostly by β^- emission (neutron ejecting a negatron and becoming a proton), while those to the left will decay mostly by β^+ emission (proton ejecting a positron and becoming a neutron), or electron capture (a K-shell electron captured by the nucleus decreasing the proton number by one and increasing the neutron number by one). All three of these decay modes can collectively be called isobaric transitions as the nuclide mass number remains constant while the *ratio* of protons to neutrons changes. Once beyond the last stable nuclide, ^{209}Bi alpha emission becomes a more common form of radioactive decay from either side of the imaginary line drawn from ^{209}Bi to ^{238}U.

In general, the further away from the line of stability a nucleus lies the more unstable is the nucleus and the shorter will be its half-life. The line of stability ends at ^{209}Bi; beyond that nuclide all nuclides are radioactive. Those elements beyond ^{209}Bi also tend to be unstable with respect to alpha emission, as well as other forms of nuclear decay. Figure 3A shows the region of the Chart

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[4] While all gamma ray emissions are isomeric transitions, the specific decay mode of IT is given to those radionuclides that have a singular emission to a ground state without cascading gamma ray emission, and have half-lives that are significant in terms of being separate from any other decay mode. Typically, the IT mode is noted when the decay half-life is more than about 1 microsecond (however there is no formalism identified for this identification process).

[5] See www.nndc.bnl.gov/chart

[6] Also note that in the Chart of the Nuclides that naturally-occurring radionuclides will also have a black bar across the top of their boxes. Thus, even though they are not stable, they are present in nature as very long-lived radionuclides or their progeny.

of the Nuclides surrounding ^{235}U. In this region there are many radionuclides that decay by alpha particle emission.

Most beta decay processes are followed by gamma-ray or X-ray emission. However, there are several radionuclides that will decay by beta emission only. Examples of radionuclides that do not emit gamma rays or X-rays and which may be expected to be found in samples after a radiological event may include ^{3}H, ^{89}Sr, ^{90}Sr, and ^{99}Tc; ^{55}Fe and ^{63}Ni are also non-gamma-emitting radionuclides but both emit X-rays.

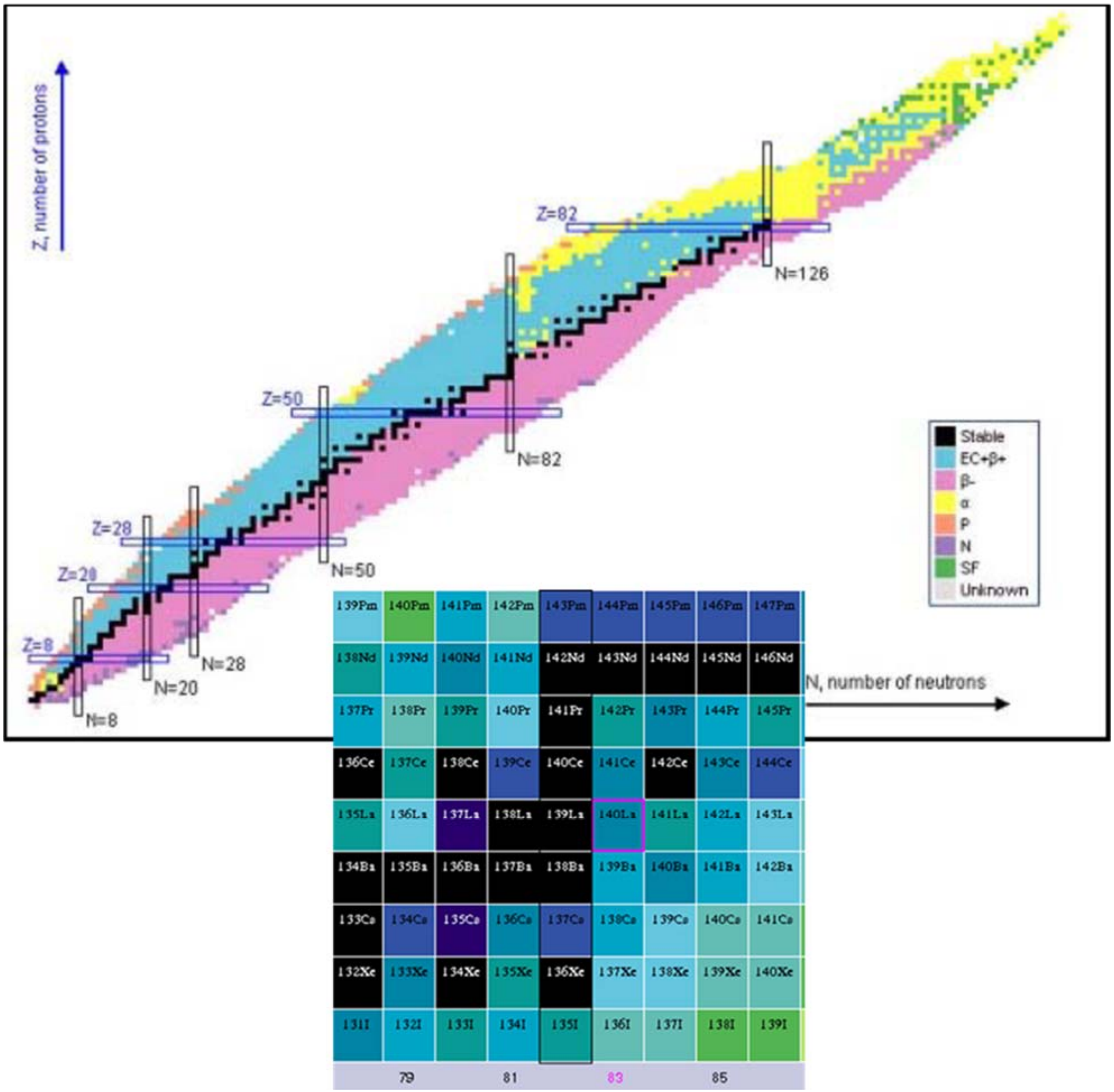

Figure 2. Line of Stability (Black Squares) and Inset (Fission Product Region for A = 131 to A = 147)

Z	233Pu 20.9 M ε: 99.88% α: 0.12%	234Pu 8.8 H ε≈ 94.00% α≈ 6.00%	235Pu 25.3 M ε: 100.00% α: 2.8E-3%	236Pu 2.858 Y α: 100.00% SF: 1.9E-7%	237Pu 45.64 D ε: 100.00% α: 4.2E-3%	238Pu 87.7 Y α: 100.00% SF: 1.9E-7%	239Pu 24110 Y α: 100.00% SF: 3.E-10%	240Pu 6561 Y α: 100.00% SF: 5.7E-6%	241Pu 14.325 Y β-: 100.00% α: 2.5E-3%
93	232Np 14.7 M ε: 100.00% α: 2.0E-4%	233Np 36.2 M ε: 100.00% α≤ 1.0E-3%	234Np 4.4 D ε: 100.00%	235Np 396.1 D ε: 100.00% α: 2.6E-3%	236Np 153E+3 Y ε: 86.30% β-: 13.50%	237Np 2.144E+6 Y α: 100.00% SF≤ 2E-10%	238Np 2.117 D β-: 100.00%	239Np 2.356 D β-: 100.00%	240Np 61.9 M β-: 100.00%
92	231U 4.2 D ε: 100.00% α≈ 4.0E-3%	232U 68.9 Y α: 100.00% SF: 3E-12%	233U 1.592E+5 Y α: 100.00% 24Ne: 9E-10%	234U 2.455E+5 Y 0.0054% α: 100.00% SF: 1.6E-9%	235U 7.04E+8 Y 0.7204% α: 100.00% SF: 7.0E-9%	236U 2.342E7 Y α: 100.00% SF: 9.4E-8%	237U 6.75 D β-: 100.00%	238U 4.468E9 Y 99.2742% α: 100.00% SF: 5.5E-5%	239U 23.45 M β-: 100.00%
91	230Pa 17.4 D ε: 92.20% β-: 7.80%	231Pa 3.276E+4 Y α: 100.00% SF≤ 2E-11%	232Pa 1.32 D β-: 100.00% ε	233Pa 26.975 D β-: 100.00%	234Pa 6.70 H β-: 100.00%	235Pa 24.44 M β-: 100.00%	236Pa 9.1 M β-: 100.00%	237Pa 8.7 M β-: 100.00%	238Pa 2.27 M β-: 100.00%
90	229Th 7932 Y α: 100.00%	230Th 7.54E+4 Y α: 100.00% 24Ne: 6E-11%	231Th 25.52 H β-: 100.00% α≈ 4E-11%	232Th 1.40E10 Y 100% α: 100.00% SF: 1.1E-9%	233Th 21.83 M β-: 100.00%	234Th 24.10 D β-: 100.00%	235Th 7.2 M β-: 100.00%	236Th 37.3 M β-: 100.00%	237Th 4.7 M β-: 100.00%
	139	140	141	142	143	144	145	146	N

Figure 3A. Thorium, Uranium, Neptunium, and Plutonium –Some Nuclear Data

Following a fission event (e.g., an IND, or power plant accident) the majority of the radionuclide fission products that will be found in samples will be from the right side of the line of stability and will be beta-gamma emitters. In Figure 3B the dark red areas indicate those radionuclides that will have the highest number of atoms formed with the number decreasing as the color changes from orange to green.

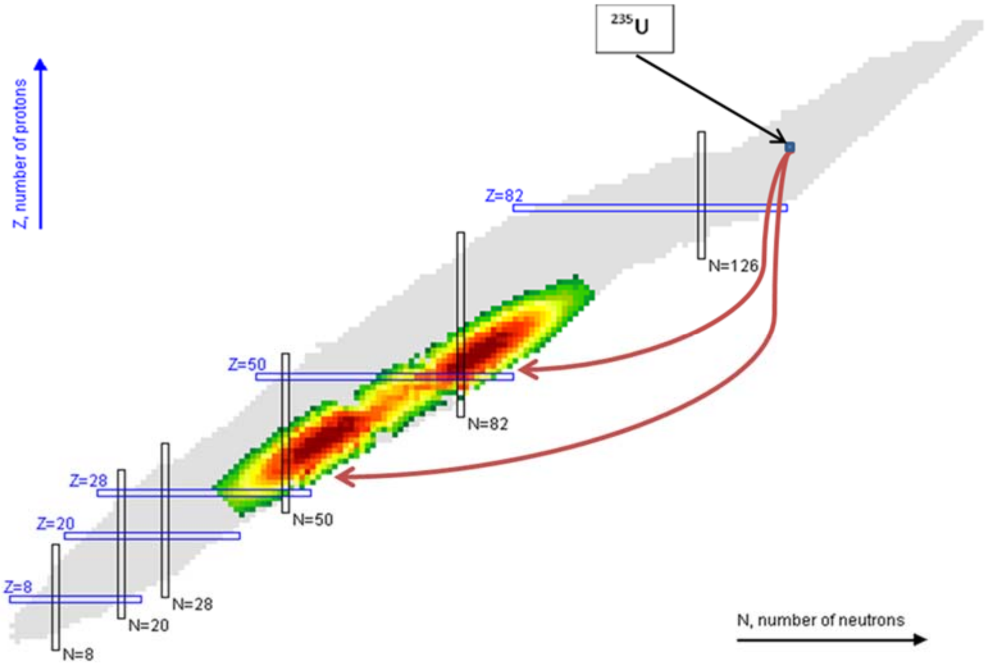

Figure 3B. The Distribution of Fission Products from ^{235}U

IV. GAMMA RAY IDENTIFICATION

A. Gamma Ray Interaction

The energy that is emitted in the form of a gamma ray is a direct result of a nuclear transition of nucleons. The gamma-ray energies most often associated with radionuclides of interest in a radiological event and which could be readily detected by gamma-ray spectrometry systems commonly in use fall in the range of the frequently used calibration standards; 59.5 keV (^{241}Am) to 1836.1 keV (^{88}Y). Operating outside this energy range (e.g., using an extended range detector) requires additional standards to extend the detection range of the detector. This will be discussed in more detail in Section J on calibration.

The three forms of gamma-ray interaction with the matter of significance in gamma-ray spectrometry are the Photoelectric Effect, Compton Effect, and Pair Production Effect. The Photoelectric Effect occurs when a gamma ray interacts with a bound electron and imparts all of its energy to the electron. The Compton Effect occurs when there is a scattering of a gamma ray after interaction with a bound electron such that the initial energy of the photon is shared between the scattered gamma ray and the scattered electron. The Pair Production Effect occurs when a photon with energy greater than 1.02 MeV interacts in the vicinity of a nucleus such that the photon is converted into a positron and an electron. Any energy greater than 1.02 MeV is distributed between the positron and electron as kinetic energy (this is discussed in more detail in Section C).

Several features will be evident in gamma-ray spectra as a result of these different gamma-ray interactions. A full energy peak is observed in the gamma-ray spectrum from multiple gamma-ray interactions with the detector in which all of the gamma-ray energy is deposited in the detector via the Photoelectric Effect (i.e., the full energy of the gamma ray is always absorbed). The Compton Effect (sometimes called Compton Scattering) and Pair Production will only produce the full energy peak if all of their subsequent interactions also occur within the detector (these are much less probable events as they involve multiple photon interactions of low cross-section in a small detector volume).

If the Compton-scattered gamma ray leaves the detector after any scattering interaction, no full energy event is recorded and the resulting signal is effectively noise (i.e., contributes to the background) at a lower energy. The collection of noise in the gamma-ray spectrum from Compton scattering is called the Compton continuum.

Figure 4 shows the relative response of an HPGe detector to gamma rays for these three effects over the energy range of 1 keV to 100 MeV.

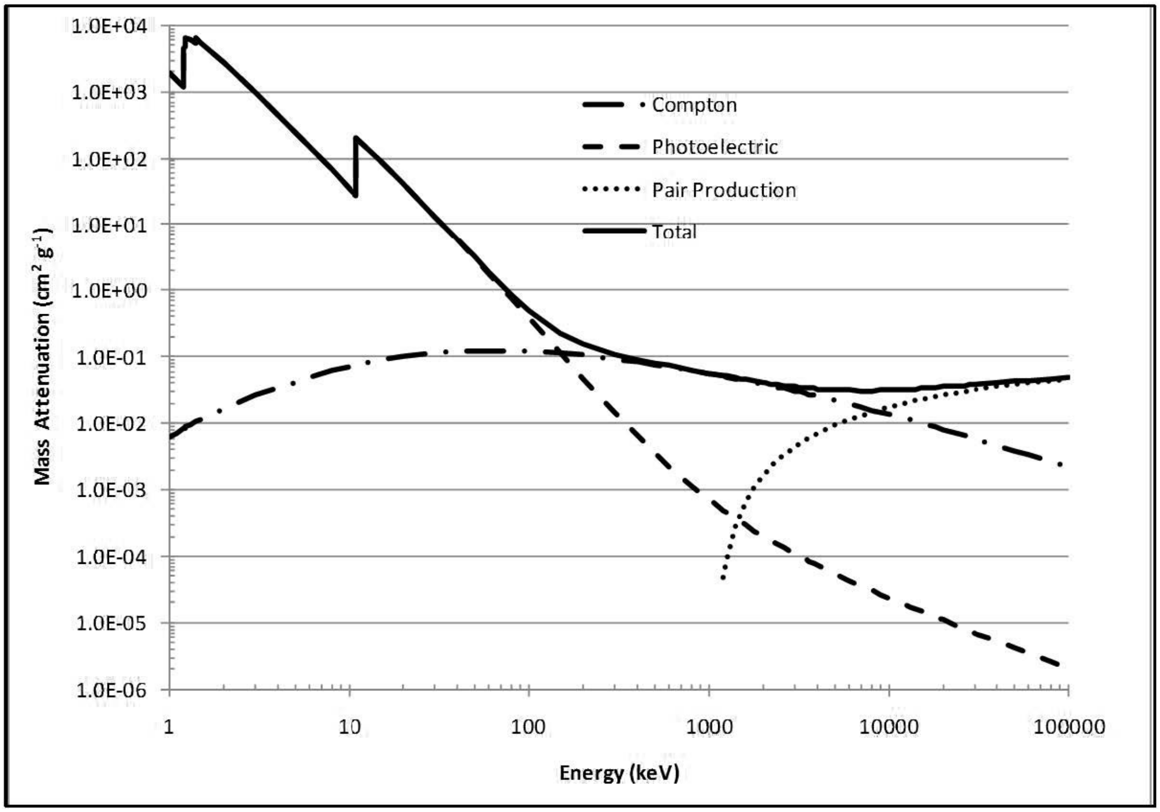

Figure 4. Probability of Interaction[7] as a Function of Energy for an HPGe

While we focus on the calibration energy range for quantitative purposes, it is important to remember that photopeaks also may be identified by the software in the quantifiable regions of the spectrum that are due to gamma-ray artifacts produced in the detector. Artifact photopeaks that occur as the result of:

- Single-escape peaks;
- Double-escape peaks;
- Summation peaks (either random or coincidence);
- Peaks within ~0.5 keV of the annihilation peak (511 keV);
- An apparent peak at a Compton edge[8];
- X-rays, especially from high-Z elements[9]; and
- Germanium x-ray escape peak 11 keV below a photopeak (in particular a low energy photopeak);

are not used to quantify radionuclide activities using only the algorithms contained in the gamma-ray spectrometry software. Software used for identification of gamma-ray peaks may have different methods of allowing the user to identify these peaks as artifacts and not use them

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[7] Diagram taken from, “Handbook of Radioactivity Analysis”, 3rd Edition, Michael F. L’Annunziata, Academic Press, 2012 (Reference 26)

[8] The Compton Edge refers to the highest energy point of the continuum. The background counts drop off precipitously above this energy (see Figure 8 for an example).

[9] Z refers to the number of protons in an element.

in quantitative peak analysis. It is critical that these user-selectable functions be understood and spectra for non-routine samples (especially those from a radiological emergency) be reviewed for their applicability to those radionuclides and activity concentrations present.

Some artifacts also may be formed by several events yielding a detector response at a specific energy in the gamma-ray spectrum, but the software determines that it has the shape and characteristics of a gamma ray. The only interaction of a gamma ray with the detector that has both quantitative and qualitative value is through the Photoelectric Effect. This interaction provides a measure of the full energy of the original gamma ray. Two other interactions of note that lead to routine features in the gamma-ray spectrum are the Compton Effect and the Pair Production Effect. Review of Figure 4 shows the relative probabilities of interactions of gamma rays with an HPGe detector as a function of energy. From low gamma-ray energy up to about 140 keV, the principal means of interaction is by the Photoelectric Effect. The Compton Effect is dominant between 140 keV and about 8,000 keV. Above 8,000 keV, pair production becomes dominant. Note that the threshold energy for pair production to occur is 1,022 keV. For several naturally-occurring and man-made radionuclides, there are gamma rays with energies in the range of 2,000 to 3,000 keV that will produce peaks (single- and double-escape peaks-see description in next section) in the energy range used in gamma-ray analysis. These may appear as unknown peaks in the gamma-ray report since these energies do not correspond to real gamma rays. In addition, the gamma-ray source of these artifacts may lie beyond the calibration range normally used. Thus, these gamma-ray energies are often not included in software libraries. Some gamma-ray software uses a “suspect library” to assist in identifying unknown peaks such as the single- and double-escape peaks and their sources. This software will assign potential radionuclide identities based on a separate library that can be used after initial analysis of the spectrum.

Calibration curves for efficiency, energy, and resolution will be discussed in more detail in Section M.

B. Potential Threat Radionuclides

Table 1 lists some radionuclides[10] that potentially could be used in a radiological dispersal device (a “dirty bomb” or RDD). Table 2 identifies radionuclides that could result from a release of fresh fission products (such as a nuclear power plant breach or an IND). These radionuclides could subsequently contaminate environmental samples in the vicinity of ground zero and downwind of the event.

Several of the radionuclides in these tables have progeny that also are radioactive. For example, if ^{241}Pu is identified, ^{241}Am likely will be present. However, the extent to which progeny may be present depends on the age of the material used in the RDD.

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[10] Radionuclides with half-lives less than about 12 hours have not been included in this list (unless they are short-lived progeny of a long-lived progenitor) as most samples analyzed by laboratories supporting the event would be days old.

Table 1. Possible Gamma Emitting Radionuclides Resulting from a Radiological Event

Alpha Emitters [1]							
Radionuclide	Gamma Energy, keV	Gamma-ray Abundance [6]	Half-Life	Radionuclide	Gamma Energy, keV	Gamma-ray Abundance [6]	Half-Life
Am-241	59.5	0.359	432.7 y	Ra-226	186.2	0.0364	1.599x10^{3} y
Cm-242	44.1	0.000035	162.8 d	Th-228	84.4	0.0122	1.91 y
Cm-243	277.6, 228.2	0.14, 0.106	29.1 y	Th-230	67.7	0.0038	7.56x10^{4} y
Cm-244	42.8	0.0026	18.1 y	Th-232	63.8	0.000263	1.4x10^{10} y
Np-237	86.5	0.124	2.14x10^{6} y	U-234	53.2	0.000123	2.46x10^{5} y
Pu-238	43.5	0.000392	87.7 y	U-235	185.7	0.570	7.04x10^{8} y
Pu-239	51.6	0.000272	2.41x10^{4} y	U-238	49.6	0.00064	4.47x10^{9} y
Pu-240	45.2	0.000447	6.56x10^{3} y	U-Nat	185.7 (^{235}U)	0.570	4.47x10^{9} y

Beta Emitters							
Radionuclide	Gamma Energy, keV	Gamma-ray Abundance [6]	Half-Life	Radionuclide	Gamma Energy, keV	Gamma-ray Abundance [6]	Half-Life
Ac-227 [2] / Th-227	236	0.129	21.7 y/18.7 d	Ba-140/La-140	537/1596	0.2439, 0.9540	12.8 d/1.68 d
Bi-212 [4]	727	0.0667	60.6 min	Mo-99/Tc-99m [3]	740, 141	0.1226, 0.89	2.75 d/6.01 h
Bi-214 [4]	609	0.455	19.9 min	Pd-103	39.7	0.00683	17.0 d
Co-57	122, 136	0.856, 0.1068	271.8 d	Pb-210 [4]	46.5	0.0425	22.3 y
Co-60	1173, 1332	0.9985, 0.9998	5.271 y	Pb-212 [4]	239	0.436	10.6 h
Cs-137[2]	662	0.851	30.0 y	Pb-214 [4]	352	0.356	27 min
I-125	35.5	0.0668	59.4 d	Pu-241[2,5]/ Am-241	59[5]	0.359	14.3 y
I-129	39.6	0.0751	1.57x107 y	Ra-228 [2] / Ac-228	911 (Ac)	0.258	5.76 y/6.15 h
I-131	364	0.815	8.01 d	Ru-106 [2] / Rh-106	511.9, 622	0.204, 0.0993	1.02 y / 299 s
Ir-192	317	0.8286	73.8 d	Se-75	265, 136	0.589, 0.585	119.8 d

Notes:

[1] The radionuclides in this table are alpha emitters generally with low abundance gamma rays. However, if any of these were part of an event (e.g., from an RDD, or a nuclear power or reprocessing plant materials) as pure radionuclides, detection using gamma-ray spectrometry could be very effective.

[2] Beta only emitter; progeny emits gamma ray.

[3] Parent is a low abundance or non-gamma emitter; progeny used for quantification by gamma spectrometry. See discussion of decay equilibria in Section E.

[4] These radionuclides are found in many environmental samples as a result of being decay progeny of ^{226}Ra or ^{224}Ra. Care should be taken in the assignment of their half-lives in gamma spectrometry libraries. See discussion of decay equilibria in Section E.

[5] The production of the $^{239+240}$Pu isotopes results in the production of ^{241}Pu as a result of multiple neutron captures. Pu-241 has a 14-year half-life. If the nuclear material is "old", measurable activity of ^{241}Am (a beta decay product of ^{241}Pu) may be present, even if this radionuclide was not originally present in the source term for an event.

[6] Abundances, half-lives, and energies were taken from the National Nuclear Data Center, Brookhaven National Laboratory, http://www.nndc.bnl.gov/chart/. Uncertainties are not included here but may be found at the referenced site.

When the alpha emitters noted in Table 1 are present in samples at normal environmental concentrations, they are best determined by means other than gamma-ray spectrometry. However, if these radionuclides are the major source of the radioactive contamination and present at high activities, gamma spectrometry (using the gamma rays noted) may be a good method of analysis. U-235 and ^{241}Am fall into the range of gamma-ray emitters where their analysis by gamma spectrometry is possible, but their abundances are relatively low compared with other gamma emitters. Additionally, when analyzing for ^{241}Am, with a gamma ray at 59 keV, special consideration should be given for matrix density (more attenuation of the gamma ray because of the low energy) and background from Compton electrons (high background in lower energy area when high energy gamma rays are present).

Several of the Table 1 radionuclides emit gamma rays (in addition to the ones shown) in the range of 29 to ~100 keV. This region of the electromagnetic spectrum also contains X-rays from the decay of fission product radionuclides such as I, Xe, Cs, Ba, La, and Ce as well as from Pb X-rays due to excitation of the shielding material from the sample gamma rays. If more than one of these radionuclides is present there will be multiple X-rays from these radionuclides which will overlap and significantly compromise the ability to make a quantitative assessment of the activity due to a particular radionuclide.

Table 2 identifies those radionuclides that would be most prevalent in fission events. While a number of these radionuclides are present as single radionuclides (i.e., no radioactive progeny) several parent-progeny pairs are shown in Table 2 (see Section E for discussion of decay equilibria). In a fission event, if the parent (listed first) is found in a sample, then the progeny eventually will be present. Depending on its gamma-ray abundance and the half-lives of the radionuclides, the progeny may be the radionuclide determined by gamma spectrometry. For example, ^{140}La ($t_{1/2}$ = 1.7 days) may be readily detected but its parent, ^{140}Ba ($t_{1/2}$ = 12.8 days), may not be detected due to low abundance of the ^{140}Ba gamma rays and its much longer half-life (i.e., lower specific activity). Also, parent-progeny pairs may not be in radiochemical equilibrium due to differences in the chemical reactivity in the environment, or the time elapsed since the event. A specific example of such an issue arises with ^{95}Zr/^{95}Nb. While their chemical similarities may keep them “together” in the environment, it takes about 180 days under stable chemical conditions for these two radionuclides to approach transient equilibrium.

Radionuclides that are “beta-only” emitters, such as ^{90}Sr/^{90}Y, may have a distinct effect on the low energy region of the gamma-ray spectrum. The effect is an increase in background counts due to bremsstrahlung and any photons produced as a result of Coulombic interactions with bound electrons. The visual result of these interactions can be what appears to be a Compton edge in the spectrum that does not correspond to any specific gamma ray.

Unless extraordinary circumstances apply, we should not assume to have control over processes in the environment (at least without stating such in the analytical report). Exceptions could include, for example, refractory or extremely insoluble radionuclide pairs in particulates/soils where it is reasonable to assume that there will be no fractionation between their formation in the event and sample collection. Once the sample is collected, however, it is presumably preserved and stored under controlled conditions to prevent fractionation from occurring.

Even when it appears that appropriate measures have been taken to properly preserve samples, the chemistry involved with mixtures of elements present in fresh fission products can be quite complex. For example, noble gasses, like Xe and Kr will emanate from the sample regardless of the type of container. Similarly, acidification will oxidize the iodide which can then be volatilized from solution. An example that demonstrates the importance of sample preservation is discussed under Figure 32 in Attachment 2.

Table 2. High-Activity Radionuclides Resulting from a Fission Event

Alpha Emitters	**Beta/Gamma Emitters**		
Am-241[1]	Ba-140/La-140	Mo-99/Tc-99m [3]	Ru-103/Rh-103
U-235 [1]	Ce-141	Nd-147/Pm-147 [2]	Ru-106/Rh-106 [3]
U-238 [1]	Ce-143/Pr-143[2]	Eu-155	Sb-125
Pu-238	Ce-144/Pr-144	I-131/Xe-131	Te-132/I-132 [3]
Pu-239 [1]	Cs-134	I-133	Zr-95/Nb-95
Pu-240 [1]	Cs-137 [3]	Np-239	Zr-97/Nb-97
Pu-241	Eu-154	Pm-151/Sm-151[2]	
Activation Products			
Co-58	Ag-110m	Cr-51	Mn-54
Np-239	Co-60	Fe-59	Na-24

Notes:

[1] Principally an alpha emitter with low abundance gamma rays

[2] These radionuclide pairs represent examples of "No Equilibrium". For instance, after approximately 70 days the ^{147}Pm activity exceeds the ^{147}Nd activity

[3] Parent is a low abundance or non-gamma emitter; progeny used for quantification by gamma spectrometry.

The activation products shown in Table 2 are the ones most likely to be associated with fission events. However, depending upon the specific source of the fission materials and location of the event other activation products for the first or second row transition series are also possible.

An RDD event may not necessarily have one radionuclide; several different radionuclides and their progeny may be present. In a fresh fission product event, activation products (such as those listed in Table 2) also may be present depending upon the type of material involved in the incident (includes both anthropogenic and natural materials).

An RDD or fission product event will produce environmental samples that have a mixture of radionuclides that varies depending on how soon after the event the sample is counted and environmental weathering or physical/chemical effects. These effects will also determine which radionuclides will dominate the activity (and gamma-ray spectrum) from the sample. Thus, the library used for analysis should be adjusted for these factors. For example, a sample taken 2 days following an IND event would be expected to have unsupported, short-lived fission products like ^{133}I ($t_{1/2}$ = 20.8 hours), ^{105}Rh ($t_{1/2}$ = 35.4 hours), or ^{97}Zr ($t_{1/2}$ = 16.7 hours) present, as well as some with much shorter half-lives than these radionuclides. However, two weeks following the event it would be unlikely for these radionuclides to be seen based on their relatively short half-lives compared to the decay time from the event.

C. Effects of High Activity Concentrations on Interferences and Identification

Samples containing high activity concentrations of radionuclides generally allow easier identification and quantification (e.g., shorter count times, smaller sample size, more distinct gamma-ray peaks above background) of those radionuclides. At the same time, however, they can also create certain problems.

Low abundance gamma rays

Gamma rays with an abundance of less than about 1% are not always listed in the libraries provided by the software manufacturer. Libraries provided by the manufacturer should never be used as received. The software manufacturer does not know what the potential applications are and cannot cover every possibility, but they supply libraries with a convenient framework for the user so that additions, deletions or edits can be made appropriate to the user's application.

However, when a sample with a very high activity is counted, gamma rays that have relatively low abundances may be detected. If these low-abundance gamma rays are not in the library, they will be classified as 'unidentified'. If they are within the energy tolerance (see page 54) they may also correspond to another radionuclide that is in the library and may be misattributed to that radionuclide.

For example, Figure 5 compares the entire listing for ^{132}I in the software library from a particular gamma-ray system[11] with part of the listing in the Brookhaven National Laboratory National Nuclear Data Center (NNDC) listing. In the useful quantification range, the software contains 27 gamma rays (1921 keV and 2002 keV are excluded as they are beyond the usual calibration energy of 1836 keV used by most laboratories), while the NNDC has 125 gamma rays. The NNDC contains gamma rays for ^{132}I with abundances as low as $7.9\text{x}10^{-4}$%. While it may not be reasonable or practicable to maintain all low abundance gamma rays in the analytical library used for radiological response-event analyses, it is advisable to add some of the gamma rays that were excluded from the analytical library to the suspect library so that the software can provide accurate indications of the possible source of these gamma rays, when they are present.[12]

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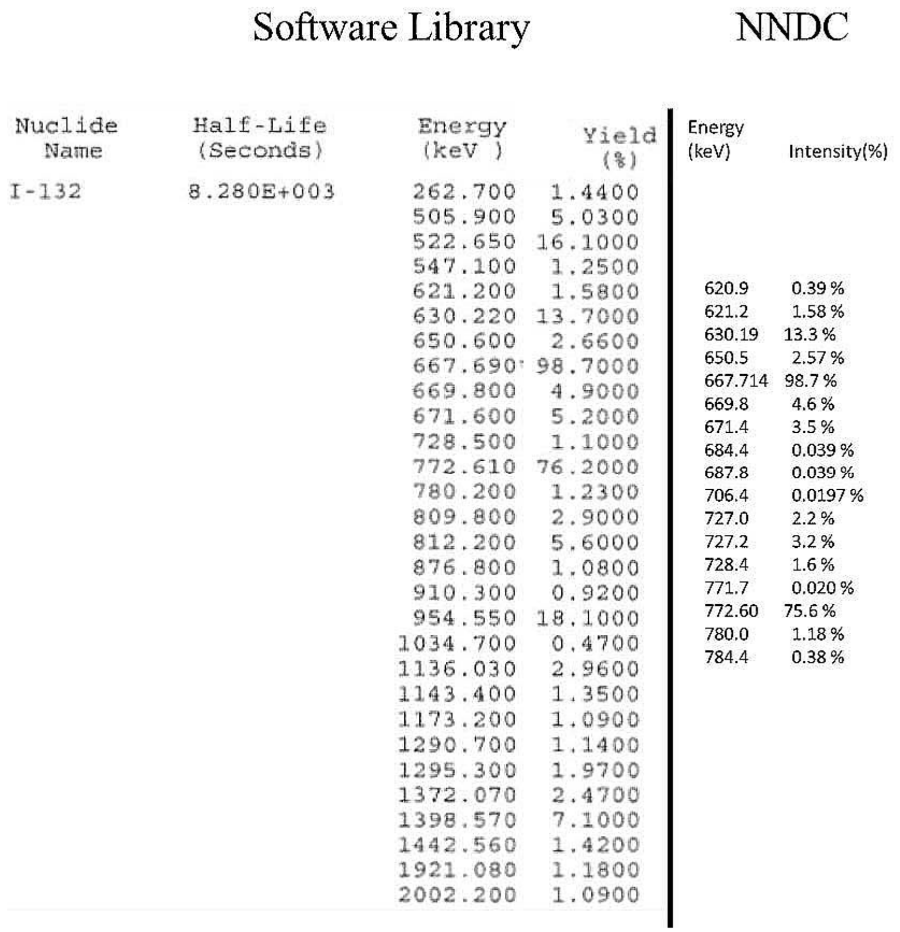
[11] Software libraries supplied with gamma-ray detection systems may not be rigidly controlled and may not be based on a recognized national or international standard reference for nuclear parameters. All libraries should be reviewed routinely ensuring that they are consistent with NNDC compilations and that undocumented changes have not been made during day-to-day use of the libraries.

[12] Using the master library as the suspect library can lead to misleading suspect identifications. Instead, the suspect library should only include radionuclides that could actually be present in samples at the time of analysis. It should also supplement the library used for the analysis of the samples. For example, the main analysis library may only need a handful of lines to properly identify a radionuclide and resolve interferences with other radionuclides present in the library. Including a longer list of photopeaks for the radionuclides in the analysis library will ensure that they are listed as suspects when higher activity samples are analyzed.



Software Library

Nuclide Name	Half-Life (Seconds)	Energy (keV)	Yield (%)
I-132	8.280E+003	262.700	1.4400
		505.900	5.0300
		522.650	16.1000
		547.100	1.2500
		621.200	1.5800
		630.220	13.7000
		650.600	2.6600
		667.690	98.7000
		669.800	4.9000
		671.600	5.2000
		728.500	1.1000
		772.610	76.2000
		780.200	1.2300
		809.800	2.9000
		812.200	5.6000
		876.800	1.0800
		910.300	0.9200
		954.550	18.1000
		1034.700	0.4700
		1136.030	2.9600
		1143.400	1.3500
		1173.200	1.0900
		1290.700	1.1400
		1295.300	1.9700
		1372.070	2.4700
		1398.570	7.1000
		1442.560	1.4200
		1921.080	1.1800
		2002.200	1.0900

NNDC

Energy (keV)	Intensity(%)
620.9	0.39 %
621.2	1.58 %
630.19	13.3 %
650.5	2.57 %
667.714	98.7 %
669.8	4.6 %
671.4	3.5 %
684.4	0.039 %
687.8	0.039 %
706.4	0.0197 %
727.0	2.2 %
727.2	3.2 %
728.4	1.6 %
771.7	0.020 %
772.60	75.6 %
780.0	1.18 %
784.4	0.38 %

Figure 5. Comparison of a Software Library (from that used at a nuclear power plant) and NNDC Database[13] for ^{132}I

When some of these low-abundance gamma rays appear in a high activity sample, if they are not in the library, they may either be misidentified as a different radionuclide or they go into the unidentified gamma rays file. When this occurs, the radionuclides associated with these gamma rays should either be manually identified the unidentified gamma rays compared to a well-constructed 'suspect' library for the sample type under analysis.

For example, the NNDC database identifies 727.0 (2.2%) and 727.2 keV (3.2%) gamma rays but the software library does not contain these gamma rays. These could be:

- Misidentified as ^{212}Bi (6.67%);
- Misidentified as ^{128}Sb (4.0%);
- Identified and the peak area used to determine all ^{212}Bi, ^{128}Sb and ^{132}I;
- Placed into the unidentified gamma rays report; or
- Potentially identified in a "suspect library."

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[13] This figure also will be referred to in Section I where mismatch of software nuclear constants and the NNDC are discussed. Note that not all the gamma-ray energies from the NNDC library have been listed in this figure.

The peak resolution would likely suffer a little as they are only 0.2 keV apart and it is not likely that they would be resolved[14]. Thus, these peaks might be rejected by the software due to high full width at half maximum (FWHM). It may be possible to resolve these peaks by adjusting the peak search or Gaussian sensitivity factor for the spectrum. In addition to these two gamma rays not appearing in the library, there is about a 30% difference in the abundance of the 728.5 keV gamma ray between the software and NNDC database value.

A critically important aspect of the software analysis to consider is that interference corrections rely on having a complete list of lines that will be present in a sample and that will interfere with other radionuclides. This would also include naturally-occurring radionuclides. For example, the 620.9 and 621.2 keV gamma rays for ^{132}I noted in Figure 5 should be included in the library as they potentially interfere with the analysis of ^{106}Ru (621.9 keV) because both are fission products.

Gamma-ray interferences not anticipated

The Compton Effect produces an “edge”[15] which is seen as a sharp decrease in the slope of the Compton continuum. If the gamma spectrometry software is not properly tuned to the performance of the detector, the software may see the Compton edge as a peak. The Compton edge occurs when Compton scattering occurs within the active volume of the detector and the scattered photon is undetected. The Compton edge is created by the maximum energy the scattered electron ($E_{e^-}^{\max}$) can have based on particle scattering formulas involving conservation of momentum, energy, and matter. The energy relationship between where the edge occurs and the gamma ray that creates that edge is derived from these scattering formulas and can be calculated using the following equations:

$$E_\gamma^{\min} = \frac{0.511 \times E_\gamma}{(2 \times E_\gamma + 0.511)} \tag{1}$$

$$E_{Compton\,Edge} = E_{e^-}^{\max} = E_\gamma - E_\gamma^{\min} \tag{2}$$

If we plot the location of the Compton Edge as a function of gamma-ray energy the curve shown in Figure 6 is obtained.

---

[14] In those instances where there are two gamma rays that will be present and cannot be resolved, it may be advantageous to use the average energy of the gamma rays and the sum of their abundances as a library entry.

[15] See Figure 8 for examples of Compton Edges.

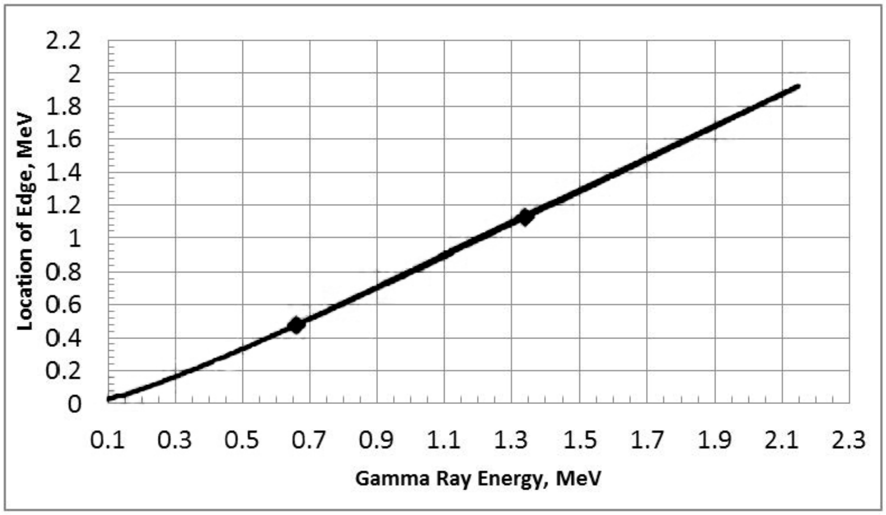

Figure 6. Compton Edge Location as a Function of Gamma-ray Energy

This curve can be of value when attempting to assess whether or not a gamma ray identified by the software is real, an artifact of the Compton edge, or interfered with by the Compton edge. This makes qualification and quantification more challenging and requires advanced software tools. For example, a peak at a Compton edge will have a significantly different background before and after the peak (leading edge & trailing edge) and will affect peak definition as well as quantification. Figure 8 shows the Compton edges associated with the two primary gamma rays from ^{60}Co. Note that although they have a significantly different shape than a gamma-ray peak, the software may identify these as photopeaks.

Another type of interference in the analysis of gamma rays appearing in the energy range of about 180 to 250 keV is the “backscatter peak”. This feature in the gamma-ray spectrum is due to a gamma ray striking an object other than the detector (usually the detector shielding) via the Compton Effect and the scattered gamma ray impinges on the detector, interacting via the photoelectric or Compton Effect. All gamma rays can interact with matter to produce backscatter radiations, which are *not* monoergic. Each gamma ray has a minimum energy for this interaction, but with multiple gamma rays of different energies, there is no exact minimum value for the backscatter peak. However, the probability of interaction of these backscatter gamma rays within the detector drops off below about 140 keV (due to the detector housing on a normal p-type detector), giving the appearance of a ‘reverse’ Compton edge (See Figure 8).

Single-escape, double-escape and multiple sum peaks

The phenomenon referred to as ‘pair production’ occurs when a photon with energy greater than 1,022 keV interacts with the electromagnetic field of a nucleus resulting in the creation of an electron-positron pair. The energy of the photon must be greater than 1,022 keV to preserve equivalence with the rest masses of the two beta particles of 0.511 keV each. Any energy greater than 1,022 keV is shared almost equally between the two beta particles as kinetic energy. Figure 7 shows the sequence of particle transformations in this event.

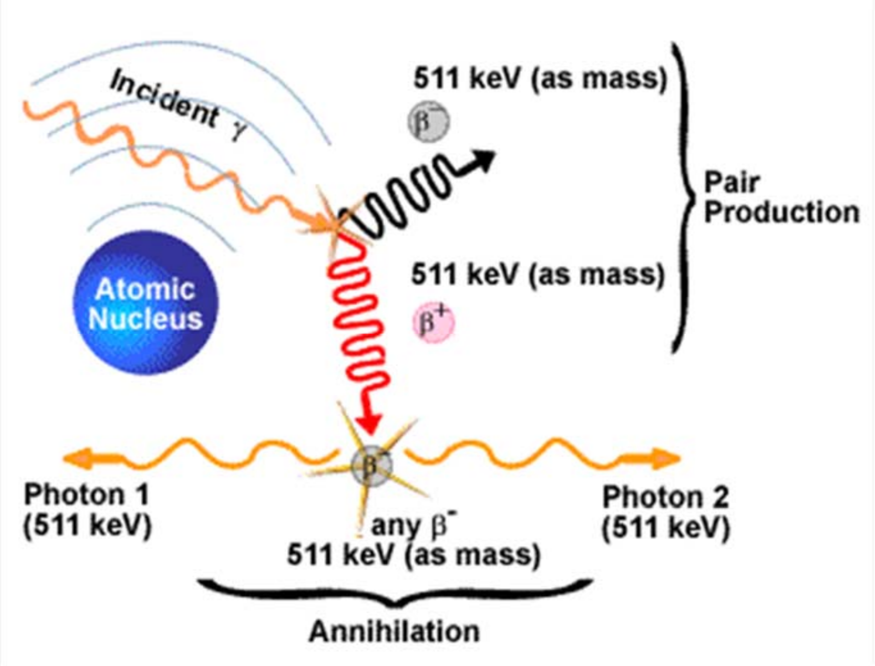

Figure 7. The Pair Production Process

Annihilation will occur when the antiparticle (positron) encounters matter inside or outside of the detector. If the encounter is made within the detector volume then it is a near certainty that the annihilation also occurs within the detector volume. When this interaction occurs within the active detector volume, two other effects can lead to features in the gamma-ray spectrum. To adequately describe these effects, it is important to note that the interaction of the gamma ray with the detector via the Photoelectric Effect produces an electron which is accelerated and amplified in the potential bias field across the active detector volume. *Any* electron produced in the active detector volume will yield a similar response. Also keep in mind that there is a finite time constant, τ, associated with the collection of charge by the detection system after a detector interaction occurs (this time constant is very long compared to the interaction). When the initial pair production occurs, 1,022 keV of the energy of the incident gamma ray is converted to negatron and positron masses with any energy in excess of 1,022 keV being converted into kinetic energy for those particles.

1. The negatron interacts with the detector during any normal Photoelectric Effect process; the negatron interacts with the atoms in the detector creating electron-hole pairs, which under the influence of electric field generated by the high voltage bias, are collected during the time frame, τ.
2. The positron undergoes a slightly different phenomenon. The positron also produces electron-hole pairs as it interacts with the atoms of the detector, then as it slows down it interacts with a single bound electron causing an annihilation event. The electron-hole pairs created, under the influence of electric field generated by the high voltage bias, are collected during the time frame, τ.
   a. At the point of annihilation, the kinetic energy of the positron is essentially zero and its collision with the electron yields two 511 keV photons, commonly referred to as annihilation radiation.

b. One or both of the 511 keV photons can interact with the detector through the Photoelectric Effect producing a photoelectron.

If processes 1, 2, and 2a occur and one of the two 511 keV photons escapes and one of the two 511 keV photons is absorbed by the detector within time frame τ, a single energy response is produced that is 511 keV less than the initial gamma-ray energy. Multiple observations of this phenomenon are referred to as a "single-escape peak" because the other 511 keV photon has escaped the active detector volume without photoelectric interactions.

If both 511 keV photons escape detection during time frame τ, then a single peak is produced with 1,022 keV less energy than the original gamma ray. Multiple observations of this phenomenon are referred to as a "double-escape peak".

A specific example of these events can be seen in Figure 8. The single- and double-escape peaks are barely visible in this spectrum, but it should be noted that the single escape peak is smaller than the double-escape peak. This is generally true even in large volume detectors, as the probability of the same initiating event causing three separate events (the initial pair production, detection of the negatron produced and the annihilation yielding a Photoelectric Effect) then creating a single response in time frame, τ, is very small.

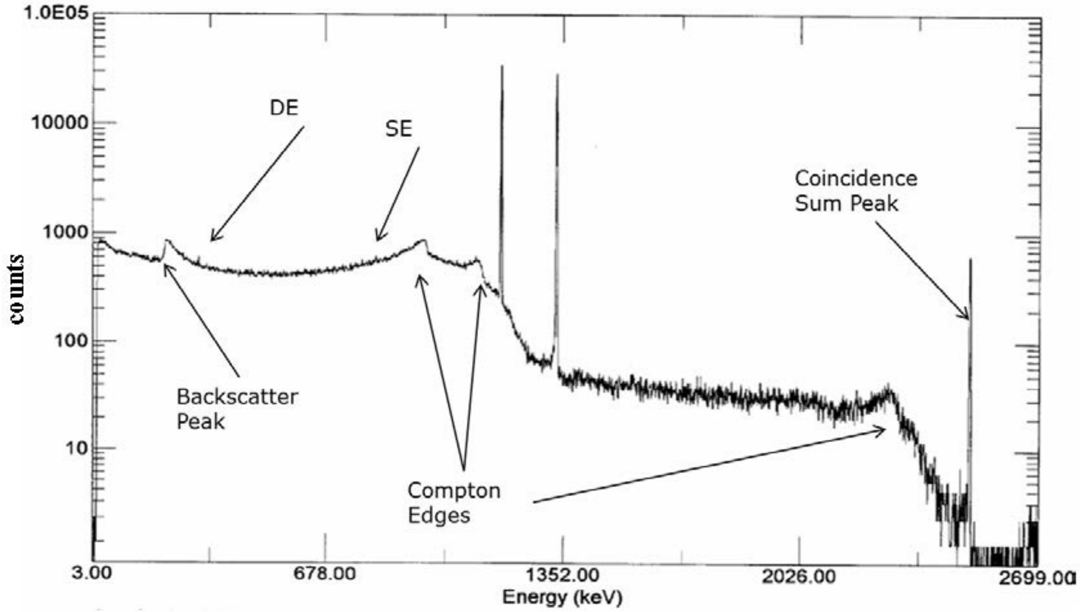

Figure 8. HPGe Spectrum of ^{60}Co (the SE and DE peaks are from the 1332 keV gamma ray)

Summing of pulses from gamma-ray interactions in the detector that arrive within the resolving time of the electronics will occur and be registered as the sum of the energies of the gamma rays. Summing is generally characterized as random summing or true coincidence (cascade) summing.

Random summing will occur for all photons that simultaneously interact within the detector giving rise to photoelectrons that are detected and processed by the electronics. A random sum peak results from two photons, most probably from twice the energy of the highest count rate gamma ray or from the two highest count rate gamma rays (from *different atoms*). If both photons of energy, E_1 and E_2, produce electrons by the Photoelectric Effect in the detector and the detection system views the total energy (as measured by the pulse size generated) as coming from a single event, then a count will be stored at the Channel (i.e., energy) where a sum peak will be recorded. The probability of summing is related to the rate of photon-detector interactions in time period τ and also to pile up pulses in the amplifier. The analog-to-digital conversion (ADC) dead time can be corrected electronically but does not eliminate the random summing problem. If the system amplifier has pulse-pile-up rejection capability this will help to reduce random summing.

Any full-energy photon that is summed with another pulse is not recorded in the single full-energy photon peak and represents a loss of counts or efficiency in that full-energy peak. This loss is count-rate dependent and therefore geometry dependent. Moving the sample farther from the detector reduces the count rate and therefore reduces the effect of random summing.

The net result of either type of summing is a decrease in the full energy count rate of each photon registered by the analyzer and an *apparent loss* of efficiency of the detector. Random summing is related to the number of pulses per unit time processed by the electronics. High activity samples counted in close proximity to the detector with high counting efficiency may produce count rates greater than 1000 cps and, subsequently, cause *significant losses* in the recorded counts in those gamma rays that are involved in the random summing effect. These losses will be a function of the energy of the gamma rays and are difficult to predict for complex spectra.

Random summing and dead time effects can be minimized by limiting the count rate to less than 1000 cps by counting smaller samples at greater distances from the detector. Older analog electronics are more sensitive to random summing effects than the newer digital electronics which may be able to process much higher count rates with minimal losses from pulse pileup.

Laboratories routinely establish acceptance limits for dead time at levels low enough to ensure that results will not be adversely impacted (e.g., 5-10%). Although most gamma spectrometry systems electronically correct for dead time, corrections for high count rates can be determined empirically to account for losses from pulse pileup. One approach involves counting a mixture of gamma-ray emitters in a fixed position with total counting rate of less than 1000 cps. The spectrum is processed to determine the count rate at each gamma-ray energy. Without moving this source, the count rate is increased by exposing the detector to a second gamma-ray source containing different gamma-ray energies than the first. The count is repeated several times adjusting the distance to the detector of the second source to yield higher count rates. The spectra are analyzed and the count rate of each gamma ray in the mixture plotted as a function of the overall count rate of the mixture to determine the effect of the increased count rate on each component of the original mixture.

True coincidence summing or cascade summing (TCS) can occur when a single atom of a radionuclide in one excited state decays from that state, and then directly to another and the lifetimes of the two excited states are very short. If the gamma rays in that cascade interact with the detector simultaneously (i.e., femto- to nanosecond time frame) compared to the resolving time of the electronics (microseconds), they will be recorded as one event at the summed energy of the two coincident gamma rays.[16]

A generic decay scheme is shown in Figure 9. The result of summing events is a lower count rate for each of the gamma rays in the cascade since a certain fraction of the events are registered as sum counts. Fewer counts are recorded for each of the cascade gamma rays (γ_1 and γ_2 in Figure 9) compared to a gamma ray of the same energy that is not in coincidence with another gamma ray. This process is referred to as "summing out". If there is a gamma transition (γ_3) from the same radionuclide that is equal to the energy of two gamma rays in coincidence then the sum peak ($\gamma_1 + \gamma_2$) is counted and adds to the total counts recorded for the independent transition. This results in a higher count rate for the independent gamma ray. This process is termed "summing in". In order to identify coincidence sum peaks, a decay scheme for each of the radionuclides identified in the spectrum should be used.

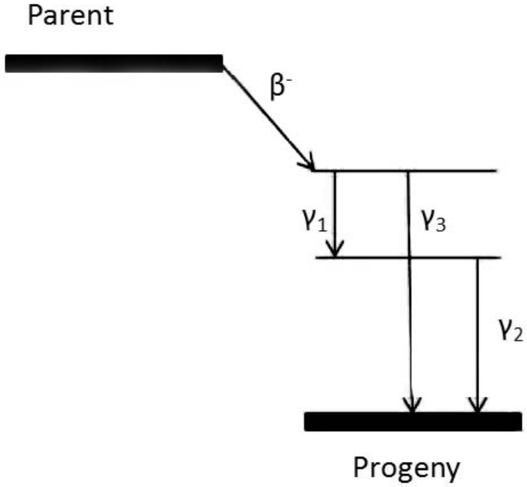

Figure 9. Coincidence decay in a beta emitter

In contrast to random summing, true coincidence or cascade summing is not a function of count rate but is related to the probability that coincident full-energy peaks of two gamma rays will be detected simultaneously by the detector. The probability of true coincidence summing is also geometry dependent and can be calibrated for directly and normalized.

This probability also is inversely proportional to the product of the efficiencies of γ_1 and γ_2. As the efficiency of detection for each gamma ray increases, the number of TCS events increases and the loss of counts in each photopeak, γ_1 and γ_2 increases. For the crossover transition, γ_3, the count rate increases with increasing *apparent* detector efficiency. This effect is highly geometry dependent (especially with regard to the size and shape of the source, and the juxtaposition of sample to detector). Any corrections made must be unique to the calibration geometry. Some

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[16] Gamma rays also sum with X-rays if the two radiations interact with the detector within the resolving time of the detection system. This effect, called γ-x summing, is pronounced in detectors that are sensitive to low-energy radiations such as X-rays. These include N-type detectors with thin entrance windows. The effect is described by Robert C. McFarland in *Demonstration of Coincidence Summing Effects Observed with N-Type Germanium Detectors in the 20- to 40-keV Energy Range When Counting ^{129}I, ^{125}I, and ^{125}Sb,* in The Counting Room: Special Edition, Radioactivity & Radiochemistry, Vol. 4, No. 2, 1993 (Reference 27).

radionuclides that are commonly encountered that display coincidence sum effects are shown in Table 3.

Table 3. Commonly Encountered Radionuclides with True Coincidence Sum Effects

Radionuclide	Gamma 1, keV	Gamma 2, keV	Sum Peak, keV
^{60}Co	1173.2	1332.5	2505.7 [1]
^{134}Cs	604	796	1400
^{154}Eu	58.4	1274	1332.8
	123.1	1047.2	1170.3
^{88}Y	1836	898	2734 [2]

Notes:
[1] Non-coincidence abundance is $2.0\text{x}10^{-6}$%
[2] Non-coincidence abundance is $7.10\text{x}10^{-1}$%

Total coincidence summing can have a significant impact on the quality of gamma-ray spectrometry measurements. Calculations of radionuclide activity should always use detection efficiencies that reasonably reflect the response of the detector to gamma rays emitted from the sample test source. The mixed gamma-ray standards that are used for routine calibrations of gamma-ray detectors will generally incorporate radionuclides with no or minimal TCS summing effects[17]. Relying on routine efficiency determinations for radionuclides with significant TCS effects will not yield accurate results.

The effects of TCS on efficiencies can be minimized, or corrections determined in several ways including the following:

- TCS can be minimized by counting samples in a calibrated geometry further from the detector (e.g., the center of the sample is at least 8-10 cm from the detector center). The increased distance between the sample and the detector may be the most practical way when measuring an unknown complex sample, especially for air filters or samples of small mass or volume. The disadvantage of this strategy is that lower efficiencies may require significantly longer counting times to reach desired detection sensitivity.
- The most accurate process for determining corrections for TCS involves empirical calibration using single-nuclide standards for each TCS radionuclide being measured. This approach is accurate and effective since the summing effects that impact the sample are exactly reproduced in a calibration standard of the same size and shape as the sample counted in the

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[17] One of the more commonly used mixtures is described in ANSI N42.14, Section B.6.2 (Reference 16). It contains ^{109}Cd, ^{57}Co, ^{139}Ce, ^{203}Hg, ^{113}Sn, ^{85}Sr, ^{137}Cs, ^{88}Y and ^{60}Co. Often ^{241}Am or ^{210}Pb are used to extend the range of this mixture. This mixture of radionuclides will result in a low bias for efficiency of monoergic gamma-emitting radionuclides in the higher energy range (e.g., Zn-65, Na-22, and Na-24).
Section B.6.3 of ANSI N42.14 recommends substituting ^{65}Zn and ^{54}Mn for ^{88}Y and ^{60}Co when counting closer to the detector than about 5 cm as is common practice for environmental samples. It may be noted that for close-in environmental geometries, when using ^{60}Co and ^{88}Y the discrepancy due to summing is generally less than about 5% (relative).

same juxtaposition to the detector. Unfortunately, this methodology may not be practical. Spectra containing many radionuclides will require having traceable sources of each of the radionuclides for which TCS is of concern.

- A third strategy is to utilize gamma-ray software that corrects for TCS effects. This option can be effective but requires special efficiency calibrations to determine the total efficiency (as opposed to photopeak efficiency) of detectors as a function of gamma-ray energy, and may require the use of dedicated libraries that are not readily customizable. Software developed in recent years may or may not require special calibrations. The user must determine which version of the software is available on their system prior to making assumptions about how coincidence summing is affected. Such corrections are also subject to interferences in complex spectra that contain interfering lines such as is common with complicated mixtures of radionuclides.
- Finally, manual calculations can be performed to determine TCS correction factors by utilizing the methodology outlined by K. Debertin and R.G. Helmer[18], or Menno Blaauw [19]. This methodology also requires the peak-to-total efficiency of the detector be determined for the gamma-ray energies being evaluated. This technique may not be practical for complex spectra with many radionuclides with TCS.

With random summing, an apparent gamma ray will be observed in the spectrum that cannot be attributed to the decay of any radionuclide and also cannot be accounted for by TCS. The random sum peak may be identified by doubling the energy of the largest peak area or adding the energies for the two largest peak areas in the gamma-ray spectrum *below* the energy of the suspected sum peak. It is possible that in samples with multiple high activity radionuclides that random sum peaks may be possible from three or more radionuclide gamma-ray emissions. While this is a less frequent event, it can still produce a small spurious peak in the spectrum. Another feature of the random sum peak is that it cannot have a Compton edge associated with it since the random sum peak energy originates within the detector as the result of a simultaneous electron production from other photon events and thus there is no way to form a Compton Effect peak.

In Figure 8, the 2505.7 keV gamma ray in the ^{60}Co spectrum is an example of a coincidence sum peak. Although the 2505.7 keV energy level goes directly to ground state its abundance is only about $2.5x10^{-6}$%. Thus, it is likely that it contributes negligibly to the observed Compton edge and that the major contribution comes from Compton interactions of the two other gamma rays occurring within the detectors time constant.

Two other examples of sum peaks are:

- In reactor coolant spectra a peak will be seen at 1321 keV from the random sum of the 810 keV ^{58}Co gamma ray and the 511 keV annihilation peak.
- In a fresh fission product spectrum, a peak will be seen at 1400 keV from the coincidence sum of the 604 and 796 keV gamma rays of ^{134}Cs.

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[18] See Reference 20

[19] "The Use of Sources Emitting Gamma-rays for Determination of Absolute Efficiency Curves of Highly Efficient Ge detectors", NIM A322, 1993, pp. 483-500 (Reference 28)

D. Decay Correction and Count Time

Ensuring correct half-life

Many references, including vendor-supplied software nuclide libraries, provide what they deem to be accepted values for the half-life of radionuclides. Inspection of these references quickly shows, however, that the half-lives vary from reference to reference as a result of the measurements selected for the evaluation. It is important to verify that the half-lives (and other nuclear data) recorded in the gamma spectrometry software library are in good agreement with half-lives identified in nationally- or internationally-recognized standards[20]. If this process is performed with the "master library" used by the software, other libraries created from the master should have reliable data.

In cases where it may be assumed that equilibrium has been fully established since the point of sample collection, the half-life of the progeny may be modified in the library to allow the software to use the half-life of the parent to make appropriate decay corrections. In those cases where it is indeterminate as to whether equilibrium is established, decay correction must be made cautiously (sometimes requiring calculations outside the gamma spectrometry software capabilities). Non-routine calculations should be disclosed in the laboratory's final report.

Decay corrections are complicated when radionuclides are members of a decay chain and are present in radioactive equilibria with a progenitor (parent). Therefore, when setting up libraries, half-lives used should reflect whether or not the radionuclide is part of a radioactive decay chain and whether the software can be used to make a decay correction. The decisions on how to establish these factors in the library should be part of the laboratory's Quality Manual for radiochemistry. This topic will be discussed in more detail in Section L.

Correction for decay during counting

Long-lived radionuclides (that decay directly to stable nuclides) like ^{137}Cs, ^{110m}Ag or ^{54}Mn will have a negligible activity change (i.e., negligible loss of atoms) over the course of a few hours between the start and finish of the counting interval. However, for many radionuclides that may be present following a radiological event, half-lives may be short, and the counting intervals used will be short (usually reflecting the urgency of needed results).

When the counting interval is greater than 10% of the radionuclide half-life a correction factor for decay during counting (DDC) should be applied[21]. If the half-life of the progeny is used rather than the half-life of the progenitor, a significant error in activity concentration of the progeny could occur, and the use of the progeny half-life to perform DDC should be noted in the case narrative.

A general formula implemented in most gamma spectrometry software for this correction is:

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[20] See References 12 or 13.

[21] For example, if a count time of 1,000 seconds is used, the DDC factor should be applied if the radionuclide half-life is less than 9,000 seconds.

$$C_f = \frac{\lambda t_c}{(1-e^{-\lambda t_c})} \tag{3}$$

Where:

C_f is the correction factor (DDC, a dimensionless quantity)
λ is the decay constant for a particular radionuclide (s^{-1})
t_c is the clock time of the analysis (s)

This equation corrects activity to the start of the counting interval. Figure 10 has plots of the magnitude of the correction factor as a function of half-life in days for three counting intervals in seconds (the plots assume zero dead time). Two different examples of how this correction factor functions are noted here:

- If a sample containing ^{134}I ($t_{1/2}$ = 52.6 min) was counted for 1 hour, the value for C_f would be ~1.45. Not applying this correction factor would result in the activity measured being ~45% low.
- On the other hand, if a sample that contained ^{132}Te ($t_{1/2}$ = 3.2 d) in equilibrium with its progeny ^{132}I ($t_{1/2}$ = 2.3 hours) was counted for 5400 seconds (1.5 hours), and the ^{132}I half-life was used to calculate the ^{132}I activity, the calculation would be biased high by 23% (a C_f multiplicative factor on the activity of 1.23 - See inset in Figure 10). Since the half-life of the progenitor is 3.2 days, the correction factor for DDC is negligible for count time of 5400 seconds (1.5 hours) or less.

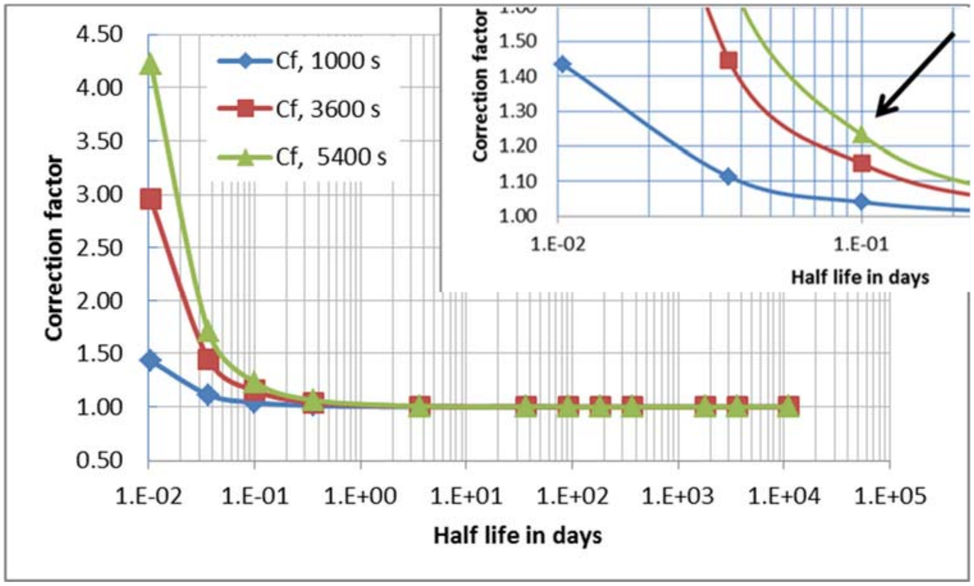

Figure 10. Correction Factor for Decay during Counting (DDC); Zero Dead Time

For gamma-ray spectrometry with no chemical separations performed, the software is able to correct the activity concentration of the sample to the start time of the analysis t_6 in Figure 13 (i.e., it accounts for the decay of any radionuclide detected during the counting interval; Figure

10). Thus, an activity concentration can be positively associated with the start time of the counting interval[22].

Adjustments to Decay Corrections Due to High Sample Activity (Correction for Dead Time)

When a sample is counted and there is measurable dead time, two-time intervals are of concern. The first is the "preset" or "live" time for the sample. This is the time period that is preselected by the user and represents only that time that the detection system is actively recording counts from the sample. Other preselect functions can be used in place of "live" time, for example counting to a preselected uncertainty or counting to achieve a particular minimum detectable activity (MDA). The second is the "real"[23] time which is the live time plus the dead time. Since sample decay occurs relative to real time, that time should be used to calculate the correction factor for decays during the counting interval.

The software used in some gamma spectrometry systems uses the live time for C_f and not the real time. Figure 11 shows the difference between using the live time (blue curve) and the real time (red curve) when calculating this correction factor. The green line shows how C_f changes as a function of dead time. These curves were generated for a radionuclide with a half-life of 15 minutes (900 seconds), a live time count interval that is 67% of the half-life and count dead times up to 13.9%. At the highest dead time for this example, the activity bias will be negative 3%. The negative bias will be most significant when the radionuclide half-life approaches the sample live times and where there is a dead time larger than about 10%.

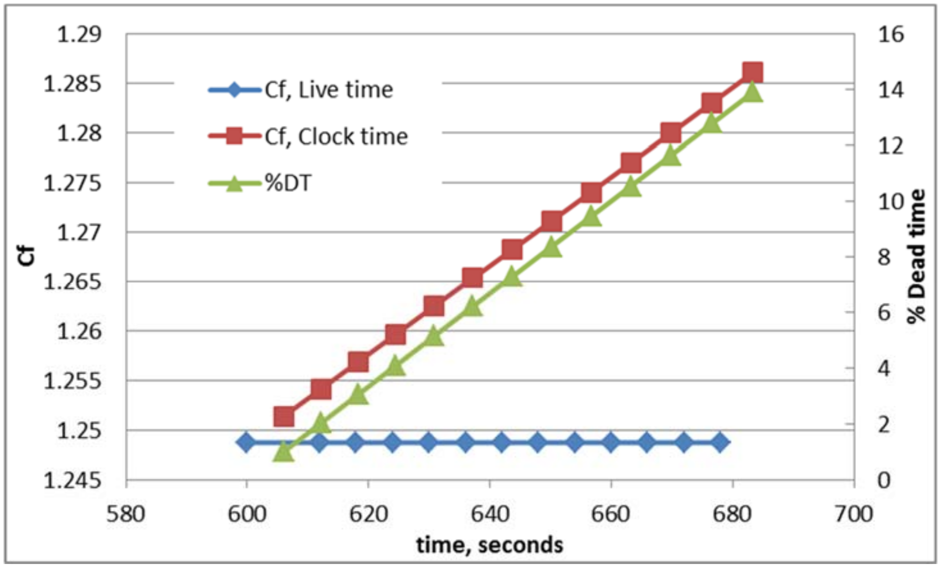

Figure 11. Correction Factor for Decay during Counting (DDC); Non-Zero Dead Time (Assumed half-life of 900 s, live time is 600 s)

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[22] This function is the decay during counting (DDC) correction, and is an option that can be selected by the user.

[23] "Real" time may also be referenced in other documents as "clock" time.

Use of the correct half-life for a progeny radionuclide when it is present at any time with its parent can lead to significant bias in the activity concentration unless the proper formulations for time decay are used for analysis. A separate issue is whether or not the library contains the correct half-life of the radionuclides; these should be checked against a national or international standards organization.

Therefore, half-lives used in the gamma spectrometry libraries should both be verified to be correct versus an accepted standard (see Reference 19 or 20) while reflecting whether or not the radionuclide is part of a radioactive decay chain. If part of a decay chain and equilibrium is established a half-life of a progenitor may be more appropriate to use in calculations (See Section L). These actions should be documented in the laboratory's Quality Manual and in the laboratory report to the client since the assumption may impact the use of the data.

The second portion of the significance of correct half-life deals with decay corrections that may need to be made back to a specific time or the time of the event to determine dose consequences *ex-post facto*.

E. Decay Correction and Radioactive Equilibrium

Three types of radioactive equilibria exist: secular equilibrium, transient equilibrium, and no equilibrium.

"*Secular equilibrium*" occurs when the parent half-life is much greater than that of its progeny. In general, once secular equilibrium has been established the activity of the progeny will equal that of the parent. Although there is no specific ratio of parent-to-progeny half-lives that defines when this relationship begins to be a secular equilibrium if the ratio[24] is greater than about 50 the difference in parent and progeny activities at equilibrium will be less than a factor 1.05 (a difference of less than 5%). Once secular equilibrium is achieved it is a useful approximation to say that the activities are "equal". An example of a radionuclide and its progeny displaying secular equilibrium is shown in Figure 12[25].

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[24] Other references provide different values for this factor. There is not a firm definition of what factor constitutes that an equilibrium is transient or secular.

[25] Note that the activity of the progeny ^{137m}Ba does not equal the ^{137}Cs activity due to branching to the ^{137}Ba ground state.

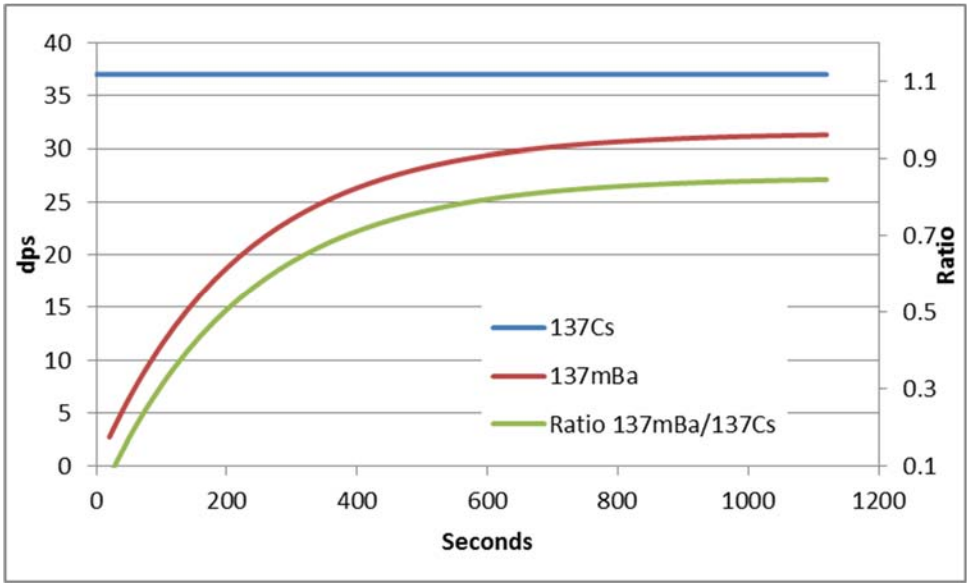

Figure 12. Secular Equilibrium Displayed by ^{137}Cs-^{137m}Ba

"*Transient equilibrium*" occurs when the parent half-life is between 1 and approximately 50 times that of the progeny (See Figure 14). In general, the activity of the progeny will exceed that of the parent once equilibrium is achieved. In these two cases, once equilibrium is established the progeny decay with the half-life of the parent as long as there are no physical or chemical effects that would separate the two radionuclides. If the activities of parent and progeny are plotted, their curves will be parallel once equilibrium is established.

In the case of "*no equilibrium*", the half-life of the parent is shorter than that of the progeny and there is no point at which the activity curves of the two radionuclides are parallel (See Figure 15).

Decay correction during counting, to a sample collection time or to event initiation can be problematic if the radionuclides are part of a parent-progeny relationship. Performing decay corrections using the "true" half-life (e.g., as listed in the NNDC database), assumes that the radionuclide is unsupported.[26] Using the parent half-life to decay correct progeny activity prior to equilibrium being established, however, can lead to bias in the decay correction unless the proper formulations for decay are used for analysis.

A second issue that needs to be addressed involves using the correct half-life to make decay corrections to a specific time, such as sample collection or the time of the event, to determine dose consequences *ex-post facto*.

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[26] Supported" refers to the dynamic situation when a parent radionuclide is present and produces new atoms of the progeny radionuclide, thereby, "supporting" its activity. The activity of the parent of a decay chain is described as being "unsupported" when no new atoms are produced and the radionuclide will decay with its "true" half-life as listed in a nuclear reference such as the NNDC database.

Depending on many factors, including the half-lives of parent and progeny, environmental conditions, or chemical effects, radionuclides that are part of radioactive equilibria may appear to decay with the half-lives of their progenitors (transient and secular equilibria). Long-lived progeny of short-lived parent radionuclides may not appear in the analysis until much after the event has occurred (No equilibrium). Since the value for activity concentration is reported at a specific date and time and since activity changes as a function of time, corrections for decay must use the half-life of the radionuclide based on sample-specific radionuclide interactions, and the sample history. When radionuclides are present following a fresh fission event where very short-lived radionuclides are present in parent-progeny relationships (like ^{132}Te/^{132}I or ^{99}Mo/^{99m}Tc,), the correct half-life will likely be that of the parent and not the half-life of the progeny.

However, even though the decay that occurs between sampling and analysis time ($t_3+t_4+t_5$ in Figure 13) may be significant, a decay correction for that interval may be performed only if the proper sample preservation occurred at the time of collection. Lacking proper sample preservation, the physical and chemical stability of parent and/or progeny radionuclides may be in question and assumptions underlying radiochemical equilibrium untenable. If the sample is successfully preserved, it is possible to determine the concentration of a parent radionuclide back to the point of sample collection using the straightforward decay correction equation (see Equation 4) implemented by most gamma spectrometry software packages.

Progeny radionuclides that are in radiochemical equilibrium relationships will need to have careful consideration of how long the decay interval ($t_3+t_4+t_5$) is compared to the half-life of the progeny[27]. If the interval exceeds the half-life of the progeny by a factor of about 5-10 (i.e., equilibrium is established), then the DDC should use the parent half-life. Figure 14 and Figure 15 are examples of radioactive equilibrium relationships. The point of equilibrium is shown as "E" on Figure 14. For decay correction prior to the "E" point, Equation 5 should be used. All assumptions made must be stated with results appropriately qualified and included in the analytics report (e.g. the case narrative).

The timeline for sample radionuclide decay from the start of the event to gamma-ray analysis is shown in Figure 13.

Performing decay corrections from the time of analysis *backward in time* may be necessary to assess potential doses to the public during the exposure period between the beginning of sampling (t_2) [28] and the count (t_6). Assuming no sample preparation/separation is performed on the sample and no chemical effects have occurred during the sampling/transport, the interval times (t_2 to t_6) in Figure 13 may be used to make decay corrections.

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[27] A special case exists for decay during air particulate filter sampling. It is normally assumed that a constant concentration occurs during sampling.

[28] Decay correction prior to the onset of sampling and the time of the event should not be attempted because environmental conditions can unpredictably separate parent and progeny radionuclides, due to physical or chemical effects (See Attachment II for examples)

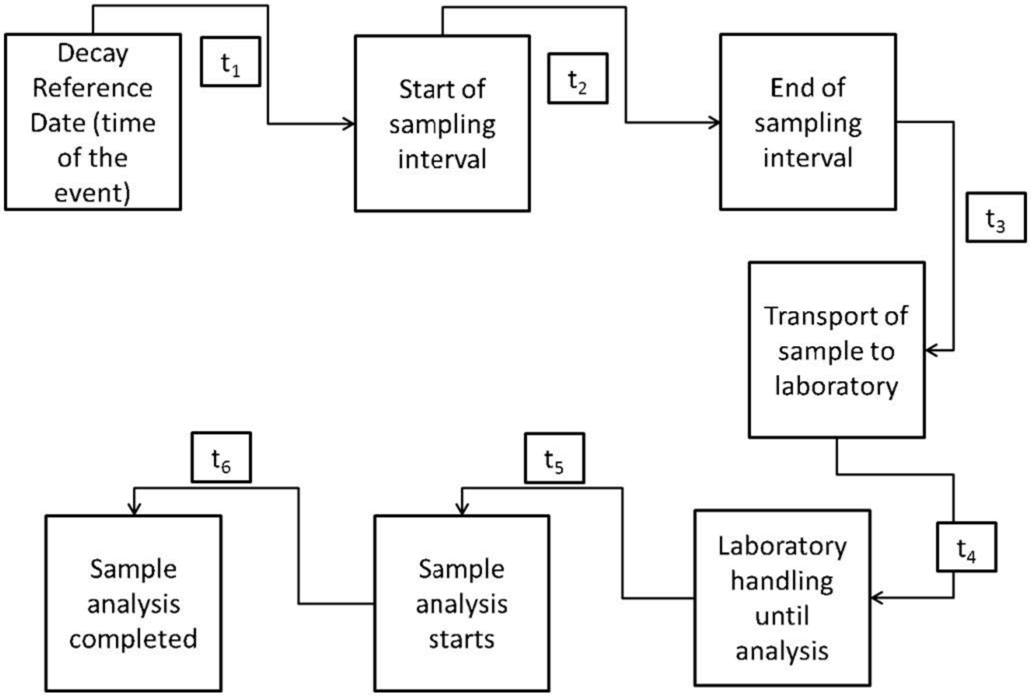


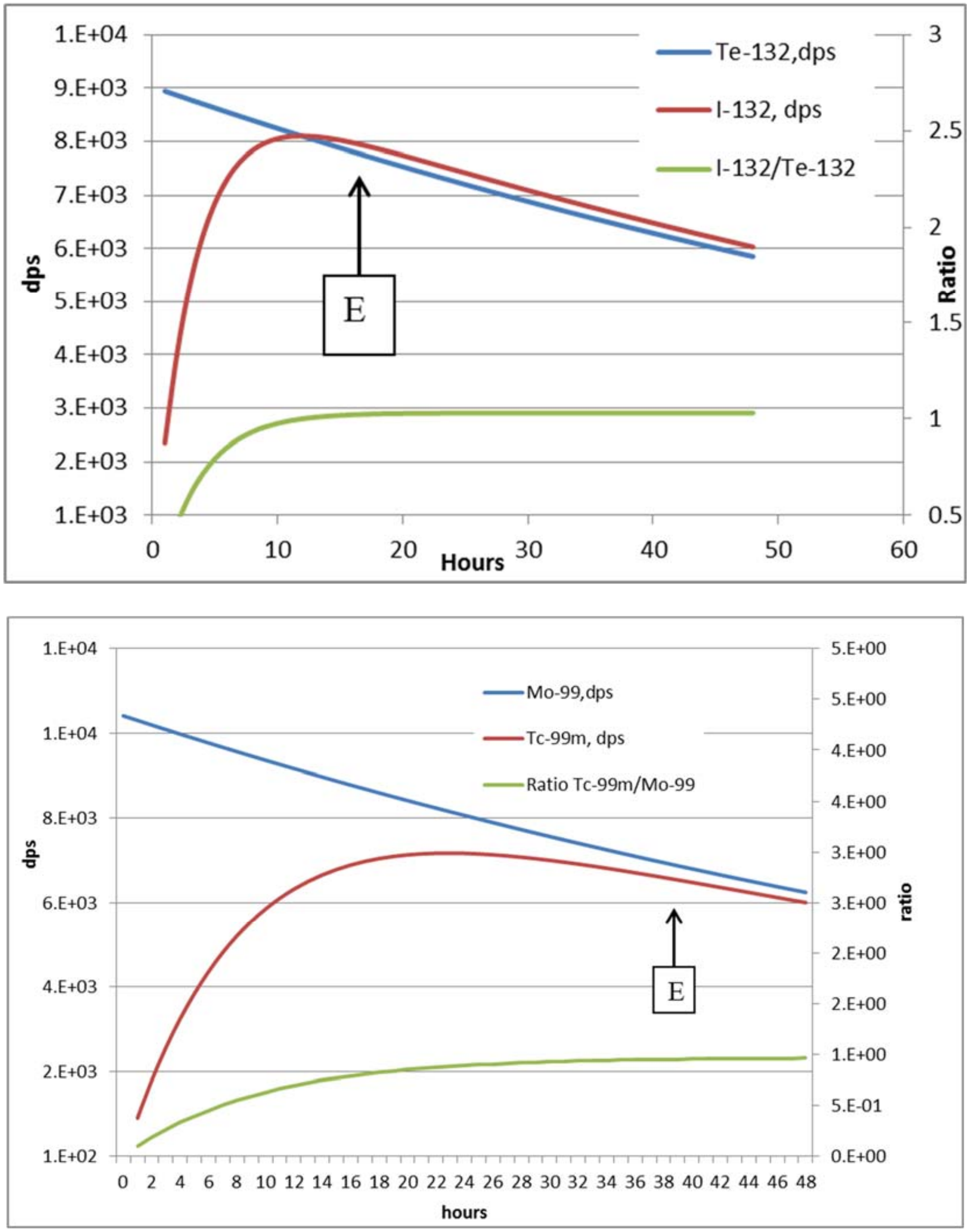
Figure 13. Timeline from Sampling to Analysis

For the specific examples of ^{132}Te/^{132}I and ^{99}Mo/^{99m}Tc, the 'as-received' software libraries usually identify the unsupported progeny half-life (^{132}I = 2.3 hours, ^{99m}Tc = 6.01 hours). A sample that is analyzed 16 hours or 36 hours, respectively, after collection will have established transient equilibrium for these two short-lived radionuclides. Once transient equilibrium is established, the activity of the progeny will decay with a half-life equal to that of the parent. This relationship is shown in Figure 14 for ^{132}Te/^{132}I and ^{99}Mo/^{99m}Tc. For the specific examples shown here, decay correction from the start of analysis backward to a time after which transient equilibrium is established simply use the decay formula

$$A_1 = A_0 e^{-\lambda t} \tag{4}$$

Where:

λ is the decay constant for the parent
A_0 is the activity at time zero (e.g., sample collection date)
A_1 is the decay corrected activity (after a time t has elapsed), and
t is the time difference between the start of analysis and the decay correction point.



Note: Even though after "E" transient equilibrium has been established, the progeny activity is less than the parent activity due to split decay modes of the parent.

Figure 14. Transient Equilibrium for ^{132}Te/^{132}I and ^{99}Mo/^{99m}Tc

In order to decay correct before transient equilibrium was established (See point E in Figure 14), a different methodology is used. Knowing the parent activity decay correction of the progeny activity back to the time prior to equilibrium being established (e.g., the sample time) can be calculated using Equation 5.

$$\lambda_2 N_2 = A_2 = \lambda_2 (\lambda_1 N_1^0) \frac{\{e^{-\lambda_1 \Delta t} - e^{-\lambda_2 \Delta t}\}}{(\lambda_2 - \lambda_1)} \tag{5}$$

Where:

λ_1 is the decay constant of the parent
λ_2 is the decay constant of the progeny
$\lambda_1 N_1^0$ (A_1^0) is the activity of parent at the initiating time sample collection
$\lambda_2 N_2$ (A_2) is the activity of progeny at the end of time interval t
N_2 is the number of atoms of progeny
Δt is the time between the event and the time to which the progeny activity concentration is being corrected

Decay correction for these equilibria prior to the sample collection time is a complicated task and would require a great deal of information about environmental conditions, the time of the event and the particular chemistry of the radionuclides with the environmental matrix.

Equation 4 and Equation 5 can be used for calculations involving transient and secular equilibria. These equations should be used with caution especially when it is not firmly established if the "E" point in the above graphs has been passed[29].

For radionuclide pairs that form "no-equilibrium" conditions a different equation may be used as shown in Equation 6:

$$A_2^1 = A_2^0 e^{-\lambda_2 \Delta t} + A_1^0 \left(\frac{\lambda_2}{\lambda_2 - \lambda_1}\right)\left(e^{-\lambda_1 \Delta t} - e^{-\lambda_2 \Delta t}\right) \tag{6}$$

Where:

A_2^1 is the activity of progeny at the time to which the activity is corrected
A_1^0 is the activity of the parent at the time of sample collection
A_2^0 is the activity of the progeny at the time of sample collection

An example of this condition is shown in Figure 15 for ^{143}Ce/^{143}Pr (33.04 h/13.57 d). Here the activity ratio of progeny to parent as a function of time never reaches plateau.

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[29] Point "E" in these graphs (and any others with these types of equilibria) is usually between 5 and 10 progeny half-lives after the onset of ingrowth of progeny. The position of "E" depends upon the half-life differences. The approach to equilibrium is exponential so there is no specific definition that states when this should occur. Generally speaking it is convenient to use the point when the ratio of the parent to progeny does not change by more than about 5%.

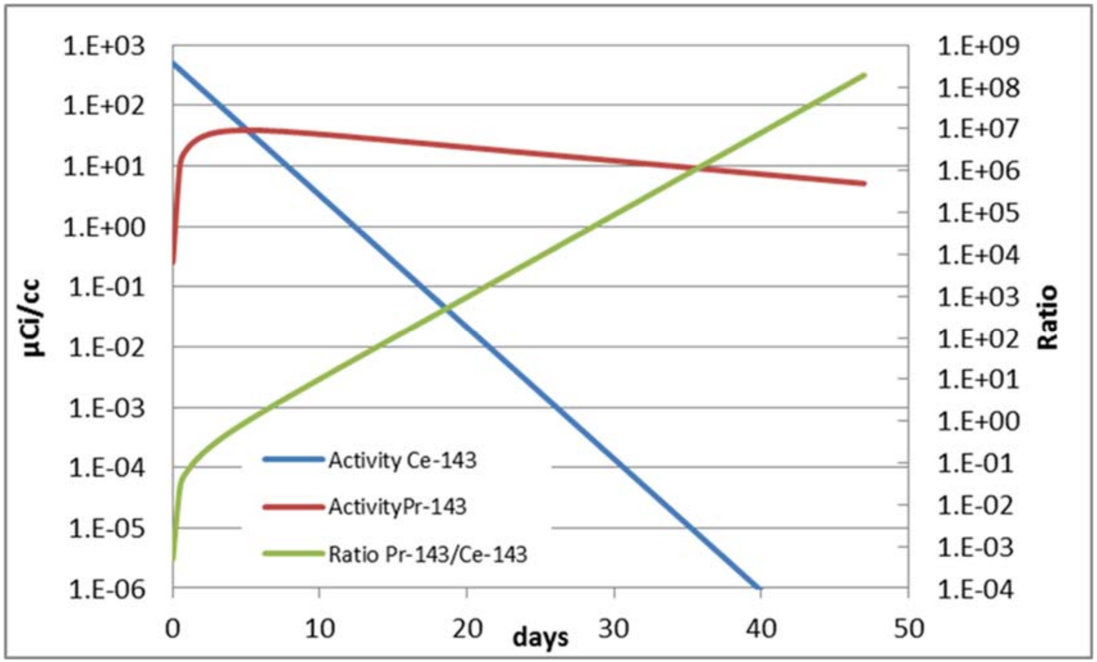

Figure 15. No-Equilibrium Case for ^{143}Ce/^{143}Pr

Within 5 days of an event, the activity of the parent is less than that of its progeny (assuming no chemical effects disturb the chemical equilibrium). If an estimate of the activity concentration for ^{143}Ce were needed 1 day after the incident using a sample that was procured 50 days after the incident (when ^{143}Ce would likely not be detected) Equation 6 could be used to make that calculation (assuming no chemical effects occurred). Generally speaking, decay correction back to the time of sampling is only possible if the sample has been properly preserved. In this equilibrium as well, decay correction prior to sampling is very tenuous as the effects of environmental weathering, etc., would need to be taken into account and these are not easily predicted for most radionuclides.

There are several important radionuclide equilibrium pairs that immediately follow a fission event (like an IND or nuclear plant accident) that are worth noting. These radionuclides and several of the naturally-occurring radionuclide equilibrium relationships (which occur in environmental samples or could result from an RDD) are shown in Table 4 along with their decay constant values and the time to achieve peak progeny activity. The equation used to calculate the time to peak progeny activity is:

$$time_{peak\ progeny\ activity} = \frac{(ln\lambda_1 - ln\lambda_2)}{(\lambda_1 - \lambda_2)} \qquad (7)$$

The time calculated in Equation 7 assumes that there were no progeny atoms present initially (i.e., radiochemically pure parent). This equation holds true for the case of No Equilibrium as well, since there is a time when the ingrowth of the progeny reaches a maximum. It should also be noted that the activity ratio of progeny/parent is calculated using Equation 5 and will be at a time that is different than the time to peak progeny activity.

Table 4. Time for Radionuclide Pairs to Achieve Maximum Progeny Activity

Radionuclide Pair	λ Parent (Days^{-1})	λ Progeny (Days^{-1})	Time to Peak Progeny Activity[c] (Days^{-1})	Type of Equilibrium	Activity Ratio Progeny/Parent Post Equilibrium[a]
Fission Products					
^{95}Zr/^{95}Nb	1.08×10^{-2}	1.98×10^{-2}	6.73x10^{+1}	Transient	2.2
^{99}Mo/^{99m}Tc[b]	0.252	2.77x10^{0}	9.52x10^{-1}	Transient	0.96
^{140}Ba/^{140}La	5.44×10^{-2}	4.13×10^{-1}	5.65x10^{0}	Transient	1.15
^{106}Ru/^{106}Rh	1.87x10^{-3}	2.00x10^{+3}	6.94x10^{-3}	Secular	1
^{132}Te/^{132}I	2.17×10^{-1}	7.30x10^{0}	4.96x10^{-1}	Transient	1.03
^{131}I/^{131m}Xe	8.64×10^{-2}	5.82×10^{-2}	1.40x10^{+1}	No	N/A
^{137}Cs/^{137}Ba	6.31x10^{-5}	3.91x10^{+2}	4.0x10^{-2}	Secular	1
^{147}Nd/^{147}Pm	6.31×10^{-2}	7.23×10^{-4}	7.16x10^{+1}	No	N/A
^{143}Ce/^{143}Pr	5.03×10^{-1}	5.11×10^{-2}	5.06x10^{0}	No	N/A
Naturally-occurring Radionuclides					
^{238}U/^{234}Th	4.25x10^{-13}	2.88x10^{-2}	8.66x10^{+2}	Secular	1
^{228}Ra/^{228}Ac	3.29x10^{-4}	2.58x10^{0}	3.48x10^{0}	Secular	1
^{228}Ra/(^{228}Ac)/^{228}Th	3.29x10^{-4}	9.92x10^{-4}	1.66x10^{+3}	Transient	1.4
^{226}Ra/^{222}Rn	1.19x10^{-6}	1.81x10^{-1}	6.59x10^{+1}	Secular	1
^{214}Pb/^{214}Bi	3.70x10^{+1}	5.01x10^{+1}	2.31x10^{-2}	Transient	3.8
^{212}Pb/^{212}Bi	1.56x10^{0}	1.66x10^{1}	1.57x10^{-1}	Transient	1.1
^{210}Pb/^{210}Bi	8.51x10^{-5}	1.38x10^{-1}	5.36x10^{+1}	Secular	1

Notes:

[a] Assumes no physical or chemical effects that disturb the equilibrium.

[b] The branching factor for the decay of ^{99}Mo direct to ^{99}Tc, of 12%, is taken from Table of Radionuclides, ISBN 2 7272 0201 6, Bureau National De Metrologie (France 1999). Calculations were performed using the Bateman equation for the parent-progeny relationship between radiochemically pure parent and daughter as direct fissions to ^{99m}Tc would not contribute to the measurements greater than 1 day after the irradiation.

[c] The time to peak progeny activity should be used with caution See Footnotes 25 and 26.

When radionuclide Secular or Transient equilibrium relationships are determined to be present after counting a sample, decay corrections for the progeny can be made *by the software* to a previous point in time, if that point in time is after the equilibrium has been established (Equation 4 would be used). If that is done, care should be used to ensure that the parent half-life is used for that correction (i.e., the library for the progeny half-life matches that of the parent).

Equation 5 can be used to calculate the activity of parent or progeny after the activity of a parent or progeny has been determined, but it assumes that there was no progeny present when the progeny ingrowth started. This equation *may be* selectable in some software packages (check the specifics of the technical information in the software manual).

To decay correct for parent or progeny in No Equilibrium relationships, or anytime the decay correction point in time precedes equilibrium for Secular and Transient Equilibrium, Equation 6 would be used: this is generally not available in the software (i.e., a calculation 'outside' the software using the activities determined at the start of the count time would be input into Equation 6 to decay correct).

Parent-Progeny Equilibrium not Established

It is important to know the time that an event occurred and to a certain extent the type of material that was used when fission products are involved since there are several different parent-progeny equilibria that can be present. Some are so rapid to reach equilibrium (as in the case of ^{106}Ru/^{106}Rh, a little more than 4 minutes) that by the time the samples reach the laboratory equilibrium can be reasonably assured[30]. Others (like the ^{143}Ce/^{143}Pr in Figure 15), are "no-equilibrium" conditions where the parent half-life is short and radionuclide progeny appear many days after the event or during remediation, without parent activity ever being measured.

There is also the concern that parent-progeny equilibrium has not yet been established; specifically earlier in time before point "E" on Figure 14. At these times on the ingrowth curve, the activity of the progeny will first increase then decrease with the parent half-life. Therefore when attempting to make decay corrections from the beginning of the analysis start time to any other time, past or future, it is imperative that the event and sample history are well established.

Parent –Progeny Equilibrium Disturbed or Created by Chemical Effects

Gamma spectrometry has the unique, purported advantage in radiochemical analysis that chemical separations typically are not needed when analyzing for gamma-ray emitters. Sample preservation of aqueous samples *beyond* acidification is often not considered important since many of the radionuclides of interest are best preserved at pH of less than 2.0.

However, some examples of radionuclides in specific matrices requiring unique preservation techniques are noted here:

- Radioiodines in aqueous matrices. Acidification will cause oxidation of iodine to I_2 which can cause loss due to volatilization or container adsorption. Samples suspected of containing radioiodines would need two samples: one should be preserved via acidification processes and one should be preserved with a slightly basic solution containing a reducing agent such as thiosulfate.
- Ra-226 in solids like concrete or soil. Many analyses rely on the radioactive equilibrium yielding ^{214}Bi (after an appropriate in-growth period) whose 609 keV gamma ray is more abundant than that of the 186 keV line of ^{226}Ra. However for the decay chain to attain equilibrium between ^{226}Ra and ^{214}Bi, the loss of ^{222}Rn during sampling, transport, and

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[30] However, this assumes proper preservation of the sample.

analysis must be prevented. Thus a technique which will uniquely (for each matrix) fix the emanated radon in place is necessary. One such technique for soil is to immerse the soil in sufficient mineral oil to just cover the top surface of the sample test source (STS) container. Radon is soluble in the mineral oil (preventing loss through emanation/volatilization) and will provide a more representative geometry for the progeny when equilibrium is established after approximately 21 days.

- Charcoal and silver zeolite canisters. These collection matrices are used to collect radioiodines or noble gases during air sampling. The canisters are usually preceded in the flow path by a small pore size particulate filter (typically about 1 μm) to eliminate particulates from interfering with the analysis of the iodines or noble gases when analyzed by gamma spectrometry. Depending on the manufacturer and style of the canister the depth of active absorbent is about 4-6 cm (Reference 22). A simple way to reduce the appearance of inhomogeneity of the sample deposition in the canister is to spin the canister just above the detector.

  For the case of the charcoal absorber, it is usually assumed that the adsorption of iodine occurs in a very thin layer (i.e., face-loaded) on the inlet side. On the surface, this is a valid assumption since the number of atoms is very, very small compared to the active adsorption sites available. However, there are other materials in the air sample that can also be adsorbed on these surfaces or may affect adsorption. High humidity or presence of organic vapors can reduce the adsorption or cause it to be more uniformly distributed (i.e., fully loaded) in the canister volume. Thus, it is important that the sampling method ensures that the radionuclide distribution on the charcoal will match the loading of the standard that is used for calibration. Additionally, since both iodines and noble gases are volatile, storage and transport of the canisters prior to analysis should ensure that they are not exposed to unnecessarily high heat environments as this may cause loss of these radionuclides.

  If the samples are collected over an extended time period (several days) or analysis is delayed for several days, the ingrowth of several progenies (e.g., ^{140}Ba, ^{137}Cs, and ^{88}Rb) may occur and be observed on the filter and charcoal/zeolite canisters. It may be necessary to consider adding some of these gamma emitters to the specific protocol library so that the lines are easily identified by the software.

  If ^{135m}Xe is present a short purge with an inert gas (like nitrogen or argon) can remove this radionuclide and its 526 keV gamma ray which yields a Compton edge at ~360 keV. Removal of that radionuclide from the sample will allow for a better baseline for the 365 keV gamma ray of ^{131}I.

- Aqueous samples with fission products and transuranic elements (TRUs). Analysis of an aqueous sample containing radionuclides like Zr, Nb and some TRUs can prove challenging. Most fission products are best stabilized by bringing the solution pH to less than 2.0. The aqueous chemistry of zirconium is such that it is best stabilized with fluoride ion. However fluoride ion can cause other elements to precipitate (e.g., both uranium and plutonium if they are in the +4 (IV) oxidation state). An example of this problem is shown in Attachment II, Figure 35. Fission products and TRUs will provide examples of preservation needs that can be unique.

Incorrect Gamma Ray Used to Analyze a Radionuclide

Many radionuclides have gamma-ray energies that are so close in energy to one another that the software may misattribute the gamma-ray activity to one or more radionuclides in the library even if only one gamma-ray emitter is present. Some software will even calculate an activity for each of the radionuclides using the same peak area more than one time. An example of this situation is seen in a sample of lettuce taken from an environmental sampling program following the Fukushima event (see Figure 29) where a 177 keV with a peak area of 148 counts is used to calculate an activity for both ^{136}Cs and misidentified ^{251}Cf).

Part of the concern here is that the software has not been properly configured to perform interference corrections. This problem can be exacerbated when too many radionuclides are included in the library that cannot be in the sample, or if interfering photopeaks from a radionuclide are not included in the library.

F. Software Preset Functions

The software available to gamma spectrometry practitioners has many user selectable preset functions. Each manufacturer uses its own terminology to describe these functions, and functionality may differ from software package to software package. Additionally, the logic and order for certain steps may vary from manufacturer to manufacturer, or even using options available within a given manufacturer's software package. Thus only generic descriptions of typical software functions are identified here. It is the individual user's responsibility to understand how the particular algorithms implemented in their software function and perhaps even more importantly, how they can, under circumstances, work at cross-purposes with one another.

Peak search sensitivity

This is generally part of proprietary algorithms developed by software manufacturers to differentiate between peaks and noise in a spectrum. The specific technique employed by the software should be described in the software manual, but generally consists of a comparison between gross observations (counts) ascribed to the peak area and counts ascribed to the background continuum. The sensitivity specified for peak analysis is generally based on the relative sample activity.

Once the software locates a peak and fits the spectral data or establishes a tentative region of interest, the software may perform a test (if elected by the user) to determine whether the peak should be considered to be present in the spectrum. One commonly used technique is the critical level test:

$$L_c = k\sqrt{B + \Delta B^2} \tag{8}$$

Where:

k is the confidence level (1.645 if 95% confidence level is used),

B is counts in the Compton continuum under the "peak", and

ΔB is the 1-sigma uncertainty in B.

(For Poisson statistics $\Delta B = B^{1/2}$, and $L_c = 2.33 x B^{1/2}$)

If the net peak area is greater than L_c then the peak is considered to be identified and will be used in subsequent calculations. Note that there are many forms of peak acceptance or rejection criteria employed by software packages, some of which include user-adjustable parameters for the acceptance criteria; it is incumbent upon the software user to understand the implications of these parameters.

The option to adjust peak search sensitivity or peak rejection criteria allows the sensitivity of the analysis to be matched to the activity in the sample being analyzed. For high activity samples, where peaks will be relatively easy to locate, a low sensitivity will minimize the false identification of numerous smaller peaks that may not be of concern to the analysis. In contrast, for low activity samples, a higher sensitivity is needed to reliably distinguish small peaks from the background.

It is the job of the gamma spectrometrist to ensure that the peak search sensitivity is properly selected to ensure that all significant peaks in the spectrum are identified. For example, specifying too low a sensitivity for an environmental sample may allow peaks actually present in the spectrum to go unidentified. This is problematic since when a peak is not identified, it may not show up in the unidentified peaks report, and review of the data output will fail to show evidence that the radionuclide is present in the sample. The best way to ensure that a spectrum has been analyzed with sufficient sensitivity involves visually inspecting the spectrum to ensure that all peaks have been identified.

The spectrometrist must also be careful that the peak search sensitivity is properly coordinated with other peak identification tests to ensure that they are not working at cross-purposes with one another. This is dependent on the specifics of the software used.

Peak uncertainty cutoff

This option allows users to specify which peaks should be used in the calculation of sample results based on their relative uncertainty. If the peak uncertainty cutoff is specified to be 100% (e.g., at two standard deviations), any peaks with a one-sigma uncertainty of less than 50% will be included in for subsequent calculations, whereas any peaks with uncertainty greater than 50% will be ignored.

While the peak uncertainty cutoff is a powerful test, if not used properly, it can work at cross-purposes with other peak identification tests such as peak search sensitivity. For example, for some applications, it may be acceptable to ignore peaks with high uncertainties (e.g., > 100%). Assume that high peak search sensitivity was selected in the hope of identifying low activity radionuclides in the sample. Simultaneously specifying a two-sigma peak uncertainty cutoff of less than 30% would be more restrictive than the peak identification test described for peak search sensitivity above (which is based on detectability) and could result in a failure to identify detectable peaks and include them in subsequent analysis of radionuclides in the sample.

While some software packages protect the user against such errors, others do not. In any case, it is always the gamma spectrometrist's responsibility to understand how the software works, to ensure that it is configured properly, and that review steps will identify issues that could compromise the proper identification and quantification of radionuclides in the sample.

Alternatively, the peak uncertainty cutoff test can be disabled and the user may instead use the critical level function to address detection based only on the critical level. The user should ensure that this is satisfactory for both the client and any regulations that are involved in the analysis.

Energy comparison

This function allows the user to select the delta energy range that will be used to conclude that a found gamma-ray peak matches the energy listed for a radionuclide photopeak in the library. The energy range is either specified as a fixed energy (keV) value or is based on the calibration of FWHM versus energy (where the match width increases as energy increases). While specific values will depend on the detection system in question, examples of each would be an energy tolerance of ± 0.5 keV or an energy tolerance of 0.6 x FWHM, respectively. An overly wide tolerance (for example ± 2 keV) will result in the inclusion of many incorrectly identified isotopes but may compensate for a less-than-ideal energy calibration (not recommended). An overly narrow tolerance (± 0.25 keV) may miss isotopes and lead to many 'unidentified lines'. Ensure proper energy calibration periodicity and monitor energy calibration control charts to assure that settings used are in accord with the observed stability of the instrument. Also be aware of vendor-recommendations for settings. For example, ORTEC specifies that the same setting be used for samples as was used for the calibration, and recommends a default setting of ± 0.5 keV with values ranging between ± 0.45 and 0.7 keV. In addition to having a good understanding of default software requirements, users should maintain good environmental controls in the lab because temperature variations (as small as 5-6 ^{o}F) and humidity changes (on the order of 15%) can affect the electronics and detector response.

Half-life period exceeded

If the time period between the time of sampling and the start time of analysis exceeds a predetermined number of half-lives (based on the specific radionuclide half-life) then this radionuclide may be rejected as a candidate since its activity is likely too low to be determined. For example, a sample is analyzed one week after a radionuclide with a half-life of 2 hours, is suspected of being present. The radionuclide would have gone through:

1 week x (168 hour/week)/(2 hours/half-life) = 89 half-lives.

Its original activity would have been decreased by a factor of 2^{89}, or 6.2×10^{26}. Generally speaking, most preset functions will default to a value of about 8 to 12 for half-lives passed, representing a decrease in activity of 256 to 4,096.

This test is useful for unsupported radionuclides or progeny radionuclides in secular or transient equilibrium when the progeny half-life is adjusted to that of the parent. Some software packages do not allow this test to be disabled; in such a case it is mandatory that supported progeny be given the half-life of the progenitor otherwise the radionuclides will not be properly identified.

Note

The Key Line and Abundance (or Fraction) Limit are tests of radionuclide presence that are redundant and should not be used together unless the user understands how the simultaneous use of these tests will affect the results.

Key Line

Many radionuclides emit several gamma rays of different abundances. Usually at least one gamma ray has a significant abundance and is interference free. Typically this gamma ray may be designated the 'key line'. The software may automatically designate the first line listed in the library as a key line, or it may have the capability of designating more than one gamma ray as a key line. If the key line(s) is selected for a particular gamma ray in the library, then the software will not identify the radionuclide as being present unless that key line(s) is found.

Ensuring Correct Gamma-ray Abundance

This nuclear constant has several terms that identify it, such as abundance, branching ratio, yield or intensity. Two commonly used definitions are:

> **Abundance** - the probability of emission of a given radiation during the decay of an atom of a given radionuclide; see intensity
>
> **Intensity-** the probability of emission of a given radiation during the decay of one atom of a given radionuclide; sometimes called abundance.

Whichever definition is used, this is a value assigned to each gamma ray and may be changed by the user (with extreme caution; independent checks should be performed prior to making changes). The abundance, just like the half-life, is an experimentally derived value. The library that accompanies the gamma spectrometry software will contain the abundance for those gamma rays that are part of the library. However, the library may not contain all of the gamma rays emitted by certain radionuclides. For example, the library may only include photopeaks with abundances of greater than 1%[31]. (See Figure 5 for the example using ^{132}I). When unidentified gamma rays appear in the gamma spectrum (especially if they have small peak areas) it may be necessary to use a library or to consult a reference that has all of the gamma rays and their abundances listed to either identify or eliminate possibilities for the radionuclide(s) that may be present.

Radionuclide libraries optimized for the type of sample or matrix

The peak search algorithm identifies the energy, FWHM and peak areas for the gamma rays it finds. It then attempts to match the located energies to those listed in a library selected for analysis of that sample. Libraries need to be selected so that those radionuclides which are most likely to be found in a particular sample are easily identified, minimizing the chances of

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[31] An exception is when the radionuclide only has one gamma ray and it is less than 1% abundant. This is a rare exception.

incorrectly identifying a radionuclide that cannot be present. As an example, a sample taken from the spent fuel pool of a reactor that has been shut down for 18 months displays a gamma ray at 657 keV. Both ^{110m}Ag and ^{97}Nb have gamma rays at that energy. However, the ^{97}Nb only has a 72-minute half-life (and does not have a long-lived parent) while the ^{110m}Ag has a 249-day half-life. Having short-lived ^{97}Nb in the analysis library used to analyze an 18 month-old sample would not be appropriate.

Abundance or fraction limit

Each gamma ray emitted by a radionuclide has an abundance (see Equation 6 above for other terms used for gamma-ray abundance) associated with it. The abundance for a gamma ray is the probability of emission of a given radiation during the decay of an atom of a given radionuclide. The abundance limit entered by the user is compared to the ratio of the abundance of the gamma rays found for a particular radionuclide to the sum of all gamma rays listed in the library for that radionuclide. If the calculated ratio does not exceed the user entered preset ‘abundance limit’ then the radionuclide is rejected and the lines moved to an unidentified or rejected lines report. This test is often incompatible with the key-line test; they perform similar functions and can work at cross-purposes and result in arbitrary rejection of radionuclides that are actually present in the sample. It should not be used with libraries that contain more than one radionuclide since it is not possible to determine a single threshold that applies to different radionuclides that contain various specific lines. An exception is a software that allows the user to set different abundance limits in the library for each radionuclide. If this option is used, however, the user must carefully consider whether the limit will reject a radionuclide even with one or more photopeaks are actually present in the library. Some software packages may not allow the user to disable this function. Thus the user must know if it is or is not being used and carefully review the radionuclides identified based on how the software functions. The process for how this is accomplished should be documented in the laboratory’s Quality Manual for Radiochemistry.

Calculating individual gamma-ray activities

The basic equation used for calculating radionuclide activity for each gamma-ray energy that is to be used for activity calculation is as follows.

$$\mathrm{C_i} = \frac{\mathrm{R_{i(net)}} \times \mathrm{C_f}}{(\varepsilon_\mathrm{i} \times \mathrm{I_i})} \tag{9}$$

Where:

C_i is the activity associated with the ith gamma ray,
R_i is the net count rate associated with the ith gamma-ray full energy peak,
ε_i is the detector efficiency at the energy of the ith gamma ray,

$$\varepsilon_i = \frac{N_i}{A_i}$$

C_f is the factor for radioactive decay during the counting interval
N_i is the net area under the ith gamma-ray peak, counts
A_i is the certified activity of the calibration standard at the ith gamma-ray peak, number of gamma rays per second

I_i is the absolute abundance for the ith gamma ray

This equation is for single radionuclides with no ingrowth contribution from a parent radionuclide and no decay correction to time t_0. The term C_f is included in Equation 9 as a reminder that if the count time is long compared to the half-life of the radionuclide (e.g., counting interval is greater than 10% of the radionuclide half-life), then C_f, must be included as noted in Equation 3.

Uncertainty-based weighted mean

If multiple gamma rays are used for calculating activity then a weighted mean activity would be reported when more than one of those gamma rays is detected.

One formula that is used for this calculation is as follows:

$$C_{avg} = \frac{\sum_{i=1}^{n}(C_i/\sigma_{C_i}^2)}{\sum_{i=1}^{n}\frac{1}{\sigma_{C_i}^2}} \tag{10}$$

Where:

C_{avg} is the decay corrected weighted mean activity
n is the number of gamma-ray energies identified and usable
C_i is the decay corrected activity for the ith gamma ray
σ_{Ci} is the standard deviation of C_i

This equation puts the emphasis on the uncertainty of the individual peak activity; the lower the uncertainty the more weight is ascribed to that gamma-ray peak. It is important that the software has resolved interfering peaks and that those adjusted peak areas determine the activities of the radionuclide whose weighted mean average is being determined.

Abundance weighted mean

Another formula for determining the weighted mean activity uses the following equation:

$$C_{avg} = \frac{\sum_{i=1}^{n} C_i \times I_{C_i}}{\sum_{i=1}^{n} I_{C_i}} \tag{11}$$

Where:

C_{avg} = the decay corrected weighted mean activity
n is the number of gamma-ray energies identified and usable
C_i is the decay corrected activity for the ith gamma ray
I_{Ci} is the abundance of the gamma ray associated with C_i

This equation puts the weighting on the abundance of the individual gamma rays.

For both methods, a statistical test in the software may also be used to identify individual activity that is an outlier from the mean. That activity would be eliminated and the mean recalculated without it. This test should be used with caution making sure that the associated uncertainty of each peak is also considered, along with resolution of interfering/interfered with peaks prior to quantification.

Detection capability

There are many formulas that have been used to describe how low an activity can be measured by the gamma-ray software. Some of these are:

- Critical Level Concentration.
- Minimum Detectable Concentration.
- Minimum Quantification Level.
- Lower Limit of Detection.
- Minimum Detectable Activity.
- Safe Drinking Water Act Detection Limit.

Each of the equations associated with these concepts, and other equations used to assess detection make certain assumptions about tolerable error rate and background factors. The user has the ability to select the detection equation to be used in a specific analysis based on the client needs. Some software allows the user to select more than one equation to be used to calculate detection and be included in the analysis report. Some software allows the user to change the coverage or tolerance factor on the detection limit or critical level calculations. Thus it is extremely important that the user review the actual equations and the influence of user-adjustable parameters and not just the word titles, to ensure the correct detection equation is used (see Section I for more details on these equations). Any of these bulleted concepts may be implemented using many different formulations – even within a single software package. MARLAP Chapter 20 goes into detail on the theory of detection. But it is still important to underscore that

Compton background determination

The gamma peaks that will be used to quantify radionuclides in a sample effectively sit “on top” of a background continuum produced by scattered Compton counts. The software must determine the fraction of counts under the peak attributable to the Compton continuum so that they can be subtracted from the total counts in that region of interest to determine the net number of counts attributable to the gamma-ray full-energy peak.

The following is a typical method used to determine the Compton background in each channel of a singlet gamma-ray peak.

The width of the peak is determined using the shape or resolution calibration of the detector. This allows the software to identify a region of the spectrum over which the total counts will be integrated to determine the gross counts under the peak. The region is bounded on the left by channel L and on the right by channel R. The average number of counts from a specified number of channels to the left side and to the right side of the peak is then used to determine the number of counts at the left and right boundaries of the peak. After this, the background in each channel under the peak, B_i, is calculated for each channel under the peak (using Equation 12 and summed to yield the total number of background counts under the peak. The background is then subtracted from the gross counts to yield the net counts attributable to the gamma ray. The algorithms used to determine the background under multiple peaks can be much more complicated.

Different software packages may allow the spectrometrist to specify the number of channels that will be used for background determination or to allow the software to make the best determination of the number of channels to use based on algorithms programmed in the software. Most modern software packages also allow the spectrometrist to visually review the spectrum to determine whether the background was adequately determined, and in some cases, to interact and modify the integration and background determination[32]. This is an important step which should always be performed to ensure that peak determinations are accurate and reliable.

$$B_i = L_{avg} + \frac{\sum_{j=L}^{i} Y_j}{\sum_{j=L}^{R} Y_j}\left(R_{avg} - L_{avg}\right) \tag{12}$$

$$L_{avg} = \frac{\sum_{i=L-N+1}^{L} Y_i}{N}$$

$$R_{avg} = \frac{\sum_{i=R}^{R+N-1} Y_i}{N}$$

Where:

i is the channel at which the background is computed,
L is the channel that defines the left limit of the peak region,
R is the channel that defines the right limit of the peak region,
N is the number of channels used in the average background calculations (limited choices but may be selected by the user),
L_{avg} is the average background to the left of the peak,
R_{avg} is the average background to the right of the peak,
Y_j is the spectral contents of channel j, and
B_i is the computed background at channel i.

A good visual of how this looks for a normal peak in the gamma-ray spectrum is shown on the next page (note that the parameter definitions in Equation 12 do not align with those in Figure 16).

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[32] See References 9 and 11

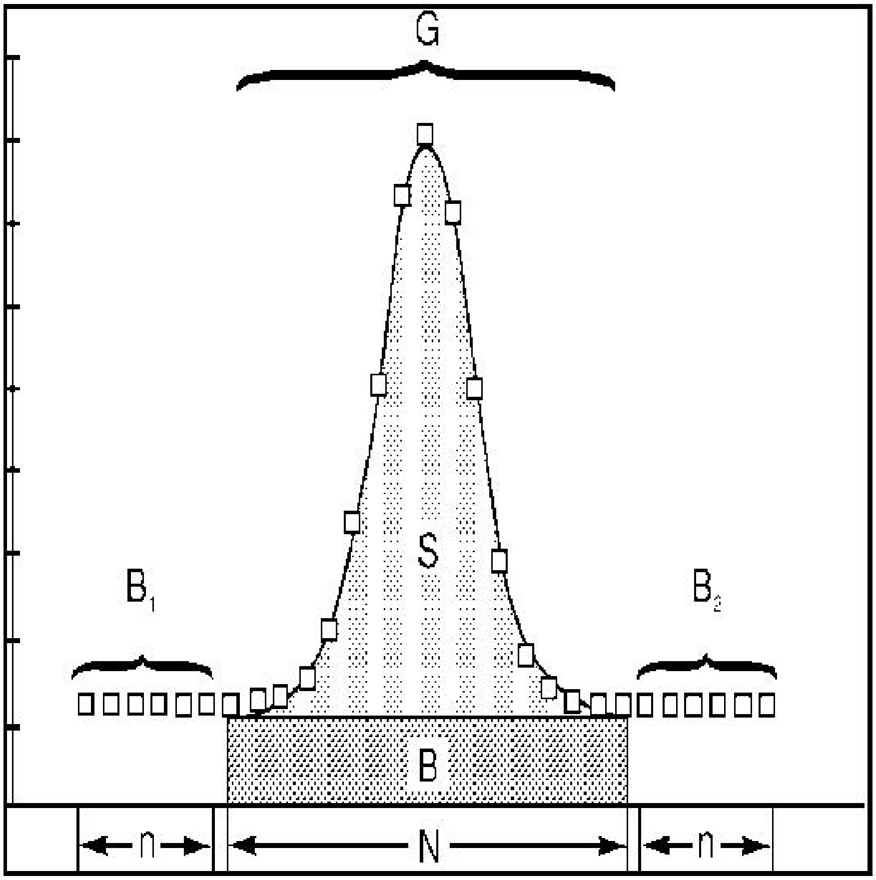

Figure 16. Method of Net Peak Area Determination

Figure 16 identifies the geometric means for determining net peak area. The variables shown in the diagram are identified as:

N is the number of channels in the peak ROI,
n is the number of continuum channels on each side (currently the same on both sides),
B_1 is the sum of counts in the continuum region to the left of the peak, and
B_2 is the sum of counts in the continuum region to the right of the peak.
S is the net peak area
G is the gross peak area and,
B is the peak background

This is an idealized picture for a gamma ray that has no interferences and does not sit on a variable background (like a Compton Edge). The software algorithms that are used to calculate the net peak area rely greatly on the calibration for resolution (FWHM), energy and low energy tailing parameters. It is beyond the scope of this document to detail these algorithms. However, it is always advantageous when complex backgrounds are present to visually review the spectrum (and if needed performing a by-hand estimate of the net peak area) ensuring that the software is adequately representing the net peak area.

Peak Background Subtraction

Compton background results from scattered gamma rays not depositing their full energy in the detector (see discussion above). In contrast, *peak background* refers to activity from radionuclides in the detector, shielding, as well as ambient gamma radiation that are able to penetrate the detector shielding to create a full-energy peak in the spectrum. It is quite common to see relatively low-activity full-energy peaks in background spectra from naturally-occurring radionuclides in shielding and detector materials, such as ^{40}K, ^{234}Th, ^{235}U, ^{226}Ra, ^{214}Pb, ^{214}Bi, ^{228}Ra, ^{228}Ac, ^{224}Ra, ^{212}Pb, ^{210}Pb, to name a few. Other peaks may also be present if the detection system has been contaminated with other radionuclides. The most common of these is the annihilation radiation at 511 keV, which cannot be used for quantification of any radionuclides since its appearance is not directly related to any individual radionuclide.

The purpose of peak background subtraction is to measure this background so that it can be subtracted from sample results. There are several different approaches used to accomplish this.

A long background spectrum is measured in a configuration equivalent to that which will be used to count samples. In cases where the sample shields the detector from radiation coming from shielding materials (or beyond), such as a four-liter Marinelli beaker full of water or milk, the background should be collected with a blank sample in place. In cases where shielding is minimal, laboratories often use no sample container at all within the detector shield to obtain a background. The duration of the background count should generally be longer than the samples being counted – often by a factor of three or more. This ensures that very low-activity peaks are well-quantified which minimizes the magnitude of bias and uncertainty associated with the correction. The background spectrum is analyzed and the full-energy peak background activity for each of the gamma rays detected is quantified. This activity is then subtracted from the peak activity of the sample spectrum prior to comparison of gamma rays to the library as part of the nuclide identification and quantification. Modern software should account for the uncertainty of the background and propagate this into an estimate of total uncertainty to be reported with the final result.

It should be noted that there may be no need to perform peak background subtraction if analysis of the long background count shows no background activity that would interfere with any of the radionuclides to be reported.

Analysis Range

One of the software settings allows the user to set the analysis range to be used when analyzing spectra. The user should keep in mind that although energy calibrations may be reliable beyond the range of the standards used for calibration of the detection system, efficiency calibrations are not. Thus, although one might be able to defend making qualitative identification of radionuclides outside the range of the calibration standards used, quantification of activity is not reliable and should not be performed. Thus the user must make a decision as to how to use the information obtained from gamma rays detected outside the calibration range.

Decay Correction

Most gamma spectrometry software packages allow the user to perform corrections for decay during counting, and to decay correct from the start of the count to a specified date in the past[33]. These decay corrections assume unsupported decay as described by Equation 3 above and can be applied a radionuclides gamma ray is detected without further consideration to radionuclides present as unsupported species in the sample (i.e., they are not decay progeny of other radionuclides in the sample). Equations are also available that describe the relationship of the decay of supported radionuclides (i.e., decay progeny) as a function of the activity of their respective parents (e.g., Equation. 4 and Equation 5).

If secular or transient equilibrium is established at the beginning of the decay period (e.g., the date of sample collection or the start time of the count), the half-life of the parent can be applied to members of the decay chain and decay correction for progeny can be made using Equation 4 as implemented in most gamma spectrometry software packages by simply substituting the half-life of the parent for that of its decay progeny in the library. As was previously stated, all assumptions made regarding equilibrium and sample preservation should be stated in the analytical report.

If equilibrium has not yet been attained by the time of the count, the activity of the decay progeny at a prior reference date cannot be calculated using most software packages, although manual calculations of the progeny activity at the reference date may be possible using Equation 13 (using the variables as defined in Section E, Equation 6).

$$A_2^0 = \frac{A_2^1 - \left(\frac{A_1^1}{e^{-\lambda_1 \Delta t}}\right)\left(\frac{\lambda_2}{\lambda_2 - \lambda_1}\right)\left(e^{-\lambda_1 \Delta t} - e^{-\lambda_2 \Delta t}\right)}{e^{-\lambda_2 \Delta t}} \qquad (13)$$

The following is an example of these calculations as applied to the activity of ^{95}Nb present on the decay correction date for a mixed fission PT sample. It also emphasizes the importance of data review as the data produced were improbable. The activity of ^{95}Zr and ^{95}Nb at the time of the count, the elapsed time between the decay correction date and the count, and the half-lives of the two radionuclides need to be known to be able to make the final calculations.

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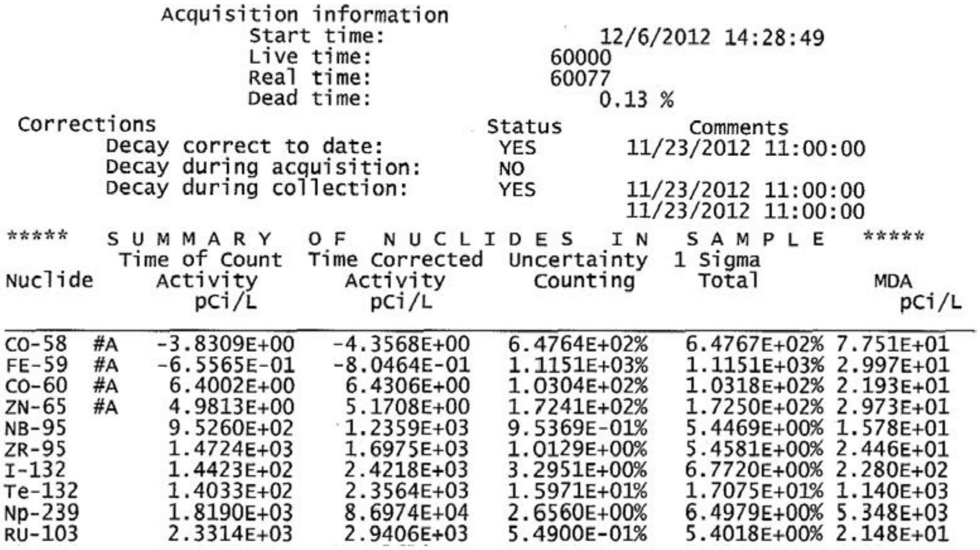
[33] Each software application is unique and it is, as always, the user's responsibility to understand the capabilities and limitations if each software application, keeping in mind theoretical limitations of these decay corrections as pointed out in this section.



```
             Acquisition information
                    Start time:                    12/6/2012 14:28:49
                    Live time:                 60000
                    Real time:                 60077
                    Dead time:                     0.13 %
 Corrections                             Status         Comments
        Decay correct to date:            YES        11/23/2012 11:00:00
        Decay during acquisition:         NO
        Decay during collection:          YES        11/23/2012 11:00:00
                                                     11/23/2012 11:00:00
*****   S U M M A R Y   O F   N U C L I D E S   I N   S A M P L E   *****
         Time of Count  Time Corrected  Uncertainty  1 Sigma
Nuclide     Activity       Activity        Counting     Total          MDA
             pCi/L          pCi/L                                     pCi/L
------------------------------------------------------------------------------
CO-58   #A  -3.8309E+00  -4.3568E+00   6.4764E+02%   6.4767E+02% 7.751E+01
FE-59   #A  -6.5565E-01  -8.0464E-01   1.1151E+03%   1.1151E+03% 2.997E+01
CO-60   #A   6.4002E+00   6.4306E+00   1.0304E+02%   1.0318E+02% 2.193E+01
ZN-65   #A   4.9813E+00   5.1708E+00   1.7241E+02%   1.7250E+02% 2.973E+01
NB-95        9.5260E+02   1.2359E+03   9.5369E-01%   5.4469E+00% 1.578E+01
ZR-95        1.4724E+03   1.6975E+03   1.0129E+00%   5.4581E+00% 2.446E+01
I-132        1.4423E+02   2.4218E+03   3.2951E+00%   6.7720E+00% 2.280E+02
Te-132       1.4033E+02   2.3564E+03   1.5971E+01%   1.7075E+01% 1.140E+03
Np-239       1.8190E+03   8.6974E+04   2.6560E+00%   6.4979E+00% 5.348E+03
RU-103       2.3314E+03   2.9406E+03   5.4900E-01%   5.4018E+00% 2.148E+01
```

Decay correction Date and Time	11/23/12 1100
Count Date and Time	12/6/12 1429
Elapsed Time (days)	13.14
^{95}Zr measured at time of count, A_1[1]	1472.4 pCi/L
^{95}Nb measured at time of count, A_2[1]	952.6 pCi/L

Figure 17. Decay Correction for ^{95}Zr-^{95}Nb

Using the data from Figure 17 and Equation 13:

$$A_2^0 = \frac{952.6 - \left(\frac{1472.4}{0.8674}\right)(2.205)(0.8674 - 0.7708)}{0.7708} = 766.8 \text{ pCi/L}$$

These results indicate that 766.8 pCi/L of ^{95}Nb was present at decay correction date (the day the sample was preserved) based on the ^{95}Zr and ^{95}Nbactivity at the time of the count. The date of irradiation of the sample was known to be 11/9/2012. Had 1698 pCi/L of ^{95}Zr been present on 11/23/2012, we could calculate that there should have been 1972 pCi/L of ^{95}Zr on 11/9/2012, and only 438 pCi/L of ^{95}Nb should have been produced by 12/6/2012 (the count date). It is also worth noting that very little ^{95}Nb is produced as a fission product (<0.1% relative to ^{95}Zr). Where did the extra ^{95}Nb come from?

Investigations showed that due to differences in their chemistry and inadequate preservation of the sample, some ^{95}Zr had been lost from the PT sample while ^{95}Nb had not (see further discussion under Figure 35). This example demonstrates the importance of:

- Reviewing the data to make sure they make sense radiochemically;
- Ensuring the proper preservation of samples; and
- Making sure to be very careful about making assumptions about the sample prior to collection and preservation.

When multiple fission events occur, a fission product and one or more of its decay products will be produced. The parent/progeny decay and ingrowth corrections employed by gamma

spectrometry software are not capable of establishing the relative amounts of each decay product at the time of fission; this calculation must be accomplished manually.
Finally, if the parent and progeny are already in equilibrium at the time of the count, and we cannot know at what point they reached equilibrium it will not be possible to (unless the progeny half-life is very short) calculate the activity of decay progeny at a point in the past, either with software or manually without the assumption that the sample was in equilibrium. Such an assumption may or not be defensible. Such decisions should always appear in the final report to the client.

Some software packages provide support that allows the user to take into account more complex radioactive equilibria, such as secular and transient equilibria. These applications are unique and it is, as always, the user's responsibility to understand the capabilities and limitations if each software application, keeping in mind theoretical limitations of these decay corrections as pointed out in this section.

As discussed above, care must be taken to consider all factors although decay corrections are performed based on the half-lives of the nuclides, and the time elapsed, other factors such as the chemical and physical stability of the radionuclides in the matrix may be critical and need to be known throughout the entire decay period in question.

Decay Build up Options

Many gamma spectrometry software packages offer to correct the results for the "build up" of activity and some of these routines apply to the activity of build up during activation analysis (which is beyond the scope of this discussion). The most common application to environmental testing is the sampling of radionuclides in air samples, to reflect the average activity present during the period of time during which the sample was collected. They generally require the date and time of the start and the completion of sample collection (note that this assumes a constant flow rate during the entire sample collection period which may not always be the case). The formula used is similar to that used for decay during counting (see Equation 3). These corrections should only be applied to unsupported radionuclide activity and not for that of decay progeny (where the parent is known to be present or must be present for the progeny to be present) unless it is known that the progeny were in equilibrium at the time they were captured in the air sample (see Example 8).

Interference Correction (Peak Overlap)

Two or more radionuclides may emit gamma rays that are located very close to one another such that their emissions would form a single peak that is a composite of the counts from each of the two peaks. Thus, is it not uncommon for a library to have what may be termed *energy duplication*. In other words, energy lines for two (or more) radionuclides may fall within the energy comparison match width specified by the user to assign photopeaks to radionuclides in the library. In the best case, the overlapping gamma rays will be minor emissions and will not be needed for quantification of the radionuclides in question and the conflict can be avoided by omitting the offending lines from the library (or better, by including them in the suspect library). When any of the gamma rays are needed for quantification, however, it is important to include all overlapping gamma rays in the library and to make sure that the interference correction option in the software is properly configured and enabled.

Gamma spectrometry software packages take a number of approaches to address library energy duplication conflicts. While it will not be possible to describe all of them, they tend to rely on a common principle. Assume that there is a radionuclide that emits a gamma ray at an energy where there may by conflicting gamma rays emitted by other radionuclides. If the other radionuclides emit other reliable (“clean”) gamma rays that are abundant enough to be accurately measured in the sample, we can calculate the contribution of counts at the duplicated energy since we know the abundance and the efficiency for gamma rays at both energies. We can then subtract them from the interfered peak area to calculate the activity attributable to our first gamma ray.

For example, given the data acquired for the spectrum in Figure 18 we see a classic example of an energy conflict between ^{226}Ra with 3.64% abundance at 186.2 keV and ^{235}U with 57.0% abundance at 185.7 keV.

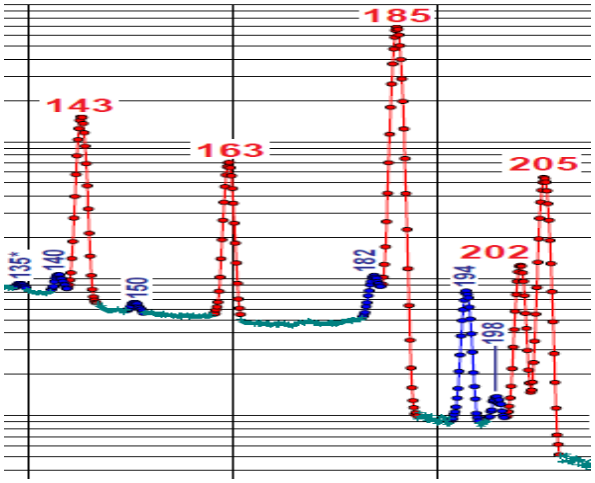


Figure 18. U-235 and ^{226}Ra Overlapping Gamma Rays

Since ^{235}U and ^{226}Ra both contribute to the peak at 185 keV (i.e., there is significant overlap of the gamma-ray energies and the peak is not well resolved), a manual determination of the individual peak areas can be made by using the secondary gamma ray of ^{235}U. The software determines that over the counting period of 2400 seconds, there are 8174 net counts in a peak at 186.0 keV. There are 1419 net counts in a peak at 143.8 keV (solely attributable to ^{235}U). The activity of ^{235}U, A_{235U}, in the sample is calculated based on the clean line at 143.8 keV as follows:

$$A_{^{235}\mathrm{U}} = \frac{R_{\text{net }143}}{\varepsilon \times I} = \frac{0.5913\ \text{counts/second}}{\left(0.0690\,\frac{\text{counts}}{\gamma}\right) \times \left(0.110\,\frac{\gamma}{\text{disintegration}}\right)} = 77.91\ \text{Bq}$$

Where:

Act_{235U} is the activity of ^{235}U
$R_{\text{net }143}$ is the net count rate in the 143.8 keV peak (counts / second)

ε is the detection efficiency (counts/gamma)
I is the gamma-ray abundance (gammas/disintegration)

Knowing the gamma-ray abundance for ^{235}U and the efficiency at 186 keV, we can calculate the contribution of counts from ^{235}U in the interfered peak.

$$\mathrm{R_{net}} = \mathrm{A}_{^{235}\mathrm{U}} \times \varepsilon \times \mathrm{I} \ = 77.91\ \mathrm{Bq} \times \left(0.0716\ \frac{\mathrm{cnts}}{\gamma}\right) \times \left(0.570 \frac{\gamma}{\mathrm{disintegration}}\right) = 3.179\ \mathrm{counts/second}$$

The contribution of ^{235}U to the 186 keV count rate is subtracted from the 186 net peak count rate. The remainder is attributable to ^{226}Ra. Now we can calculate how much ^{226}Ra is present.

$$\mathrm{A}_{^{186}\mathrm{Ra}} = \frac{\mathrm{R_{net\ 186}} - \mathrm{R}_{^{235}\mathrm{U}}}{\varepsilon \times \mathrm{I}} = \frac{3.406 - 3.179\ \mathrm{counts/second}}{\left(0.0716 \frac{\mathrm{cnts}}{\gamma}\right) \times \left(0.0364 \frac{\gamma}{\mathrm{disintegration}}\right)} = 87.1\ \mathrm{Bq}$$

Where:

$\mathrm{R_{net\ 186}}$ = net count rate in the 186 keV peak (counts/second)
$\mathrm{R_{net\ 235U}}$ = count rate in 186 keV peak from ^{235}U (counts/second)

Clearly, this is a simple example designed to show the underlying principles involved in interference corrections. Modern gamma spectrometry software packages can accommodate much more complex situations, including multiple interfering radionuclides and propagation of uncertainty associated with the corrections. It is important to understand how specific interference correction schemes work and to correctly configure the software. This includes ensuring that any libraries used to calculate interference corrections include all interfering radionuclides and peaks.

One weakness of such an approach is apparent from this example. The 143.8 keV gamma ray in this example is significantly less abundant than the 185.7 keV gamma ray for ^{235}U. Unless there is enough activity in a sample to quantify ^{235}U, no correction may take place (if ^{235}U is not detected). Similarly, the levels of uncertainty introduced into the corrected value depend on the levels of uncertainty in the measured ^{235}U activity. Unfortunately, the software will not generally point this out to the user, so checking interference corrections during the review of the final results is important. One method of determining if results for activity from different gamma rays agree is using a statistical test such as the relative error ratio (RER) or a Z-score test[34]. These have validity in that they take into account the uncertainty of the measurements, and not merely based on an arbitrary percentage.

The second concern with peak overlap and how the software "views" the overlap is the function of peak deconvolution. The software may actually perform the deconvolution, but it may automatically assign the closest energy to both peaks as opposed to really resolving the interference.

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[34] See Volume III f Reference 7.

TCS or True coincidence summing

The coincidence or cascade summing effect was described in Section IV.C. Most software does not have a provision for doing this unless the system has been calibrated with a special source and with a true coincidence calibration method. Some software attempts to correct for this using some mathematical formulations. The best way to present this is by example using a radionuclide that exhibits this effect: ^{60}Co.

Figure 19 shows an example spectrum.

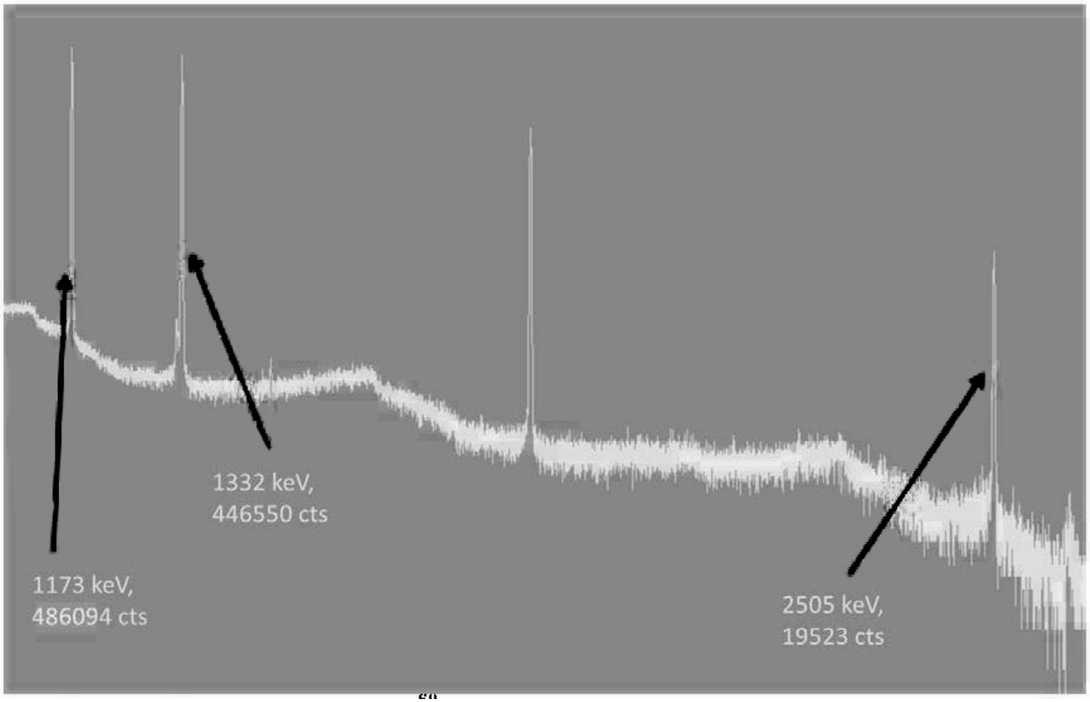

Figure 19. A Spectrum of ^{60}Co Showing Peak Areas (y-axis is log-scale)

One method of calculating coincidence correction is to make the assumption that all the counts in the sum peak came equally from the two peaks that make the summed energy. One-half of the counts from the summed peak is added to each of the lower energy peaks after they are corrected for the separate efficiencies of the two energies. While this accounts for the majority of the loss of counts, it creates an indeterminate bias.

However, coincidence correction is most effectively accommodated by specific calibration (See Reference 27 for details).

Directed Fit

"Directed fit" refers to an option used for analysis and reporting of results that is most frequently used to support environmental monitoring programs where a value is calculated for a radionuclide at a library energy even though a peak is not detected by the software. These calculated values should be reported together with their associated uncertainties even when the activity for the measurement may yield results that are not detectable (i.e., the result may be positive, negative or zero). By not censoring values (i.e., reporting "less than" or "ND" as a result), a series of measurements close to background can be averaged over time which may facilitate quantification of very low levels of activity, or detection of changes in very low levels of activity before they become detectable in individual measurements.

The process used by the software establishes a region at the energy where the peak would normally be present (e.g., three times the width of the calibrated FWHM centered on the peak energy). A background is calculated across this region and then subtracted from the integrated total counts for this region. The net count rate thus determined, together with the detection efficiency, abundance, and any other corrections (e.g., decay correction, sample size, etc.) are used to calculate an activity and an associated uncertainty.

The preset functions noted above may need to change with the type of sample, the type of radiological event, and the radionuclides being analyzed. Some generic issues where the functions have either misidentified or not identified a radionuclide are described in general here (with specific examples are shown in Attachment II).

Suspect Library

The library selected for analysis of the gamma-ray spectrum, sometimes called the "analytical" library, is usually a subset of the main software library that has been edited to contain radionuclides of concern and information that is needed to support the analysis (e.g., lines needed to perform interference corrections that also reflect the half-lives for those radionuclides that are in radioactive equilibrium). Gamma rays that are not contained in the analytical library, however, are often observed in spectra. Gamma-ray spectrum reports should always contain a section that lists all gamma rays that do not correspond to those in the analytical library (i.e., "unidentified" gamma rays). Most software packages also have a separate library, sometimes called the "suspect" library that assists the analyst in establishing the identity of unknown gamma rays in the spectrum. This should be a library that has been optimized to the type of sample being analyzed. It generally contains all possible photopeaks for any radionuclides listed in the analytical library (overlap is not problematic), as well as information for non-target radionuclides that may possibly be present in spectra, along with information that will assist in identifying spectral anomalies (e.g., sum, escape or non-target background peaks). Since the suspect library is not used for the analysis, it may be updated and maintained as needed without risking the integrity of the analytical library or negatively impacting results.

Alternatively, the stored spectrum can be reanalyzed using a different or newly created library that addresses the diversity of radionuclides contained in the samples analyzed during a specific event.

Nuclide ID Confidence

This is a calculated parameter. The radionuclide listed in the library must have at least one gamma-ray energy within the user-selected energy tolerance of a peak identified in the spectrum. For each gamma-ray energy of a radionuclide in the library that is within the energy tolerance of an observed photo-peak, the nuclide confidence value (which starts out as 1.0) is multiplied by a penalty function that reduces the value to less than one. The penalty function includes the following factors: all the gamma rays associated with this radionuclide in the library, the abundance of each of these gamma rays, the deviation of the measured energy from the library listed energy the energy tolerance used in the gamma spectrum analysis and the MDA in the measured spectrum for each of the gamma rays for that radionuclide. This function should be used with caution for several reasons:

- A low activity sample with a radionuclide that has multiple gamma rays will get a low confidence ID even though it is present.
- Gamma rays from other radionuclides that may be close in energy can cause the ID confidence of a different radionuclide to be significant when the second radionuclide is not present.
- There is no exact value for the ID confidence that can be used for detection purposes.
- Depending upon how the library is configured falsely high ID confidence values may be recorded.

Ultimately it is the responsibility of the reviewer to ensure that the gamma rays used for the ID confidence factor are appropriate for that factor (see Examples 3 and 15 in Attachment II).

G. Selecting detectors

Bigger is not always better. For samples where we expect to find very low activity concentrations of only a limited number of radionuclides, a larger volume detector would be of benefit because it will have a greater efficiency of detection. A greater efficiency may lead to either smaller sample or a shorter count time (or both) to achieve the required detection level. However larger detectors generally will have a wider FWHM (i.e., poorer resolution) than a smaller detector. Therefore it is necessary to ensure that the radionuclides to be determined will have gamma rays of sufficiently different energies so that the poorer resolution will not affect detection (although in recent years this has improved with digital filter technology). Also note that larger detectors suffer from higher levels of true coincidence summing (depending upon the radionuclides being analyzed), especially when samples are counted close to the detector such as will likely be done to optimize sensitivity.

Larger detectors may also have higher Compton background at lower energies due to an increased probability of interaction with scattered high-energy gamma rays, and gamma-ray peaks will be slightly wider.

Conversely, for high activity samples with multiple radionuclides, it would more likely be necessary that high resolution (i.e., small FWHM) is needed so that gamma rays close in energy can be easily resolved.

A second decision that laboratories must make is between P-type coaxial detectors, with good response in the mid-to high-energy range, or extended-range N-type coaxial detectors with thin entrance windows (e.g., carbon-fiber or beryllium) and good response at low-energies. While it may be tempting to conclude that having better response across all energies is better, this may not result in selecting a detector that is optimal for the measurements a lab needs to make. Since N-type detectors are sensitive to low-energy radiations, they suffer elevated rates of true-coincidence summing, especially gamma plus X-ray summing. This will impact the accuracy of measurements unless the laboratory takes the effort to perform single-nuclide calibrations, or they implement true-coincidence summing corrections, both of which can be costly and time-consuming. The thin entrance windows are also notoriously fragile and can break leading to expensive and time-intensive detector repairs.[35] For this reason, unless the laboratory needs to use the detector to make sensitive measurements below 60-80 keV (e.g., ^{210}Pb, ^{129}I, ^{55}Fe, etc.), the extended range of the detector may not be needed or could even be deleterious. If the laboratory is planning on performing low-energy measurements, it should perhaps look into planar detectors (or other low-profile configurations) that are sensitive to low-energy photon radiations but have much lower backgrounds than coaxial detectors and are thus the best-suited detectors for low-energy measurements.

H. Sample preparation

The sampling process is not addressed in this manuscript as there are separate documents that deal with these practices for many different matrices. Also not addressed in this document is a methodology for screening samples from a radiological event. This particular issue is addressed in "Radiological Laboratory Sample Screening Analysis Guide for Incidents of National Significance" (see Reference 13).

However, once the sample is obtained, the process of preservation and preparation of the sample for gamma spectrometric analysis needs to consider the different radionuclides that may be present and their potential chemical and physical forms. Samples obtained following a radiological event such as an IND or RDD will likely contain discrete radioactive particles (DRP). The physical and chemical nature of radionuclides in a sample containing DRPs will be significantly different from those radionuclides found in environmental sampling. The high temperature from the devices will cause some radionuclides to fuse with other materials such as sand, metals, even plastics, creating a small particle that contains a very high activity of one or more radionuclides. If these DRPs exist as suspended particulate in water samples, they cannot be dissolved simply by adding acid, and their distribution in the solution may be questionable due to settling or surface attraction to the container walls. Thus, sample preparation may need to consider filtration, fixation of the material in suspension (by addition of a gelling agent) or something else.

Sampled solids may also suffer from lack of homogeneity. A method has been developed for homogenizing soil samples (see Reference 12).

Air particulate filters will generally have their pore size specified in sampling documents. During radiological events, it is possible that the particulate loading of the filters will be elevated above normal. The mass of material captured on these filters and the average Z value of those particulates will determine if correction factors for self-attenuation are required as compared to the standard used to calibrate the detector. This type of information should be requested by the laboratory of the incident command sampling group so that corrections can be made if warranted.

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[35] Detectors with thin entrance windows can and should be protected, except when being actively used for low-energy measurements. While plastic covers are often used to this ends, graded end caps composed of layers of copper and tin have been used to both protect the fragile end cap while minimizing gamma-x summing by reducing the number of low-energy radiations that can reach the detector.

It may be necessary to assess whether or not a silver zeolite or an iodine charcoal cartridge is face- or fully loaded. Most calibrations assume these cartridges as face loaded in a thin film on the absorber's surface (the side facing the air flow into the housing). Transferring the sorbent material to a secondary container after homogenizing, or counting the canister on its side, and flipping or rotating the sample half-way through the count have been used to minimize bias. Laboratories should have specific instructions on how to perform these options.

Climactic conditions such as heat, humidity, and presence of other non-radioactive, absorbable gasses may prevent the radiological kryptons, xenons, or radons from forming a thin film on the inlet to the canister. In addition, the presence of high activity concentrations of the noble gases may have a negative impact on the detection limit for ^{131}I as there may be increased background around the principal peak at 364 keV. A slow short purge with nitrogen or argon can help to remove the radioactive noble gases and reduce background in the gamma-ray spectrum.

Samples other than liquids or air particulate and charcoal cartridges may need to be prepared by grinding, sifting, or gelling, and be analyzed as wet, dry, or as received. The event authority will need to specify what the appropriate method of reporting these activity concentrations is. In general sample preparation must be carefully considered for any matrix that potentially contains DRPs.

I. Selecting Geometries, Counting Containers, Detection Equations, Count Intervals and Uncertainty Equations

Detector Geometries

HPGe detectors have shielding that cannot be easily reconfigured. Thus the sample-to-detector geometry needs to fit inside the shielding. Generally, a container as large as 4-liter Marinelli beakers can fit within the shield. A very important aspect of sample placement geometry is that the sample container should never touch the detector; the detector is not a sample stand. A sample holder or sample geometry made of low Z material should always be used to offset the sample from the detector surface. The best reasons for this offset for the sample will include at least some of the following:

- Cascade summing effects are minimized
- Probability of detector contamination is minimized
- Sample mass will not 'push' the detector cold finger into the cryostat
- Sample does not act as a 'heat sink' for the liquid nitrogen (or the new "cryo-coolers") via contact with the detector housing.

Using low Z material for fixed counting geometries minimizes attenuation by the Photoelectric and Compton Effects so that more gamma radiation reaches the detector. Plastics such as high-density polyethylene, Delrin™, Lexan ™, or polycarbonate are most frequently used. Plastics like polyvinyl chloride (PVC), Teflon™, Tefzel™ or other polymers containing halogens should be avoided as these elements raise the average Z value of the material.

1. Sample Counting Containers and Sample Size
    a. Standards containers (i.e., working calibration sources, WCS) used to calibrate the detector need to have the same volume, geometric configuration, and composition as

those containers that will be used to count samples. As with the counting geometries, the sample containers should be of a material that has low Z value. Container sizes should be selected so that the routine mass or volume of sample can be accommodated and match closely to that of the WCS.

b. Sample size and counting interval (see next section) are important considerations when evaluating the detection limit that is needed to be achieved. The basic equation for activity concentration is:

$$A_c = \frac{(N_T - N_B)C_f}{\varepsilon \times V \times t \times I \times e^{-\lambda \times \Delta t}} \tag{14}$$

Where:

A_c is the activity concentration, Becquerels per mass or volume
N_T are the total counts for the gamma-ray peak
N_B is the Compton background counts for the gamma-ray peak
C_f is the correction factor for decay during counting (DDC)
ε is the efficiency with which gamma rays are detected from the geometry in question
V is the sample volume or mass
I is the gamma-ray abundance
t is the live time
λ is the decay constant for the radionuclide, and
Δt is the time interval between sampling and start of counting

Optimizing a counting geometry to obtain the best limit of detection involves balancing several factors. As the sample size increases, the limit of detection generally decreases (i.e., the signal-to-noise and sensitivity improve). However, as the sample size increases, the geometric shape of the STS increases and the average distance of the sample to the detector increases. As the average distance increases (depending on the matrix and density and the energy of the gamma ray, the efficiency may also decrease due to self-absorption) efficiency decreases with the inverse square of the distance, and fewer net counts per unit sample mass or volume will be recorded. The number of counts collected for a given gamma peak plateaus as the size of the sample approaches "infinite thickness"[36]. At infinite thickness and beyond, increasing the sample size results in no net increase in photopeak signal (counts). In fact, if the matrix being counted contains other radionuclides (e.g., soil), increasing the sample size may result in a net loss of sensitivity since, although the efficiency may plateau, the background continues to rise from the Compton interactions of the other radionuclides (see discussion of uncertainty and MDC below).

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[36] Infinite thickness is the point at which gamma rays from the sample are absorbed within the sample and no longer can reach the detector. This "thickness" depends also on the energy of the gamma ray and is generally larger for high-energy gamma rays than for low-energy gamma rays.

Counting Interval and Detection Equations

The measurement quality objectives (MQOs) required by both normal operations and incident response will need to specify the detection limits to be achieved and most importantly the required method uncertainty for the analyses. There are many different terms used for detection. Four of these terms will be described here with equations often used to implement them, and a comparison of how the values for each differ.

It is important to note that while we identify a detection capability, it is the numerical result of an analysis obtained from measurements, along with its associated uncertainty, that should always be reported. Terms such as "Not Detected (ND)", "<MDC", "<LLD", or < (value of MDC or LLD) should not be used as these terms often misrepresent the result of the measurement and prevent the user (or client) from independently interpreting the true results of the measurement (this will also be discussed in the section on reporting).

It is noted that all the equations cited here assume a 5% tolerable error rate for Type I error (determining activity is present when it is not) and Type II error (determining that activity is not present when it is). There are other interpretations and other tolerable error rates that can be selected for detection equations. It is recommended that the reader refers to MARLAP (Chapter 20) for a more complete discussion of detection criteria and general formulas used to implement these concepts of detection.

Critical Level Concentration (L_c)

The definition of critical value from MARLAP[37] is:
"In the context of analyte detection, the minimum measured value (e.g. of the instrument signal or the analyte concentration) required to give confidence that a positive (non-zero) amount of analyte is present in the material analyzed. The critical value is sometimes called the critical level or decision level."

In the discussions that follow the critical level and other detection formulas, equations from different software packages have been included. Not all the equations have parameters defined in exactly the same way and are not directly comparable. The equations may also provide different final units from the calculations, so the user must ensure that the proper pre-set selections in the software output the desired units. Each equation is referenced to its specific source.

If the critical level is measured for a specified mass or volume of sample the result is referred to as the critical level concentration, L_c. Figure 20 shows two distributions of results; one for a blank sample and one for a sample that has detectable activity. In this figure, σ_o and σ_1 represent the standard deviation of the true blank and sample distribution.

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[37] See Reference 7.

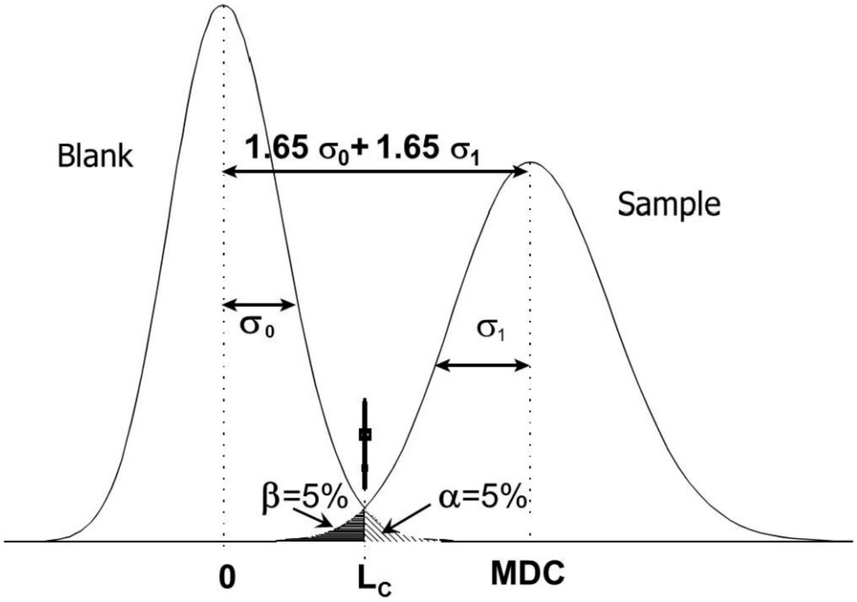

Figure 20. Distribution of Results for a Blank sample and Sample with Detectable Activity

A commonly used formula for the critical level concentration[38] is:

$$\mathrm{L_c} = 2.33 \times \frac{\sqrt{\mathrm{B}}}{\mathrm{t} \times \varepsilon \times \mathrm{A} \times \mathrm{V}} \tag{15}$$

Where:

B is the background counts
t is the live time
ε is the detector efficiency at the gamma-ray energy
V is the sample volume or mass
A is the gamma-ray abundance

The final units for L_C from this calculation will be in Becquerels per unit mass or volume. The critical level concentration is a sample specific determinant of activity concentration (i.e., an *a posteriori* determination) based on a true blank having “zero” concentration and measuring the sample-specific value for “B”. In gamma spectrometry, the sample Compton background is used to determine the L_C.

The critical level concentration (Lc) can also be defined as “the smallest concentration of radioactive material in a sample that will yield a net count (above background) that will be

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[38] The critical level, as calculated here, assumes that count time used to determine the background activity is equal to that of the sample. This is the case in a routine gamma spectrometry measurement where the background subtraction is determined from the same spectrum as the sample. If peak background subtraction is performed, however, the background should be determined from a separate count of duration at least equal to, but generally significantly longer, than that of the sample.

detected with a 95% probability."[39] This definition is more closely aligned with that of the MDC (see next paragraphs).

Minimum Detectable Concentration (MDC)

A general formula[40] for the minimum detectable concentration is shown in the next equation.

$$\mathrm{MDC} = \frac{L_D \times C_f}{t_c \times \varepsilon \times A \times V \times k_w \times k_x \times F \times U_f} \qquad (16)$$

Where:

L_D is the twice critical level plus the square of the tolerable error rate,

$$L_D = 2 \times L_C + \left(z_{(1-\alpha)}\right)^2$$

ε' is the attenuation corrected efficiency
F is the sample mass/volume conversion factor
V is the volume or mass
A is the abundance factor for the gamma ray
C_f is the correction for decay during counting
k_w is the decay correction from the start of the count time to the time the sample was obtained.
t_c is the live time
U_f is the unit conversion factor from Bq to the desired units (e.g., pCi)
k_x is the correction for decay during sample accumulation time.

The final units for MDC from this calculation would be, for example, pCi per unit volume or mass. A definition of MDC that is commensurate with the above equation is:

> "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."

Figure 20 displays the location of a series of measurements that would represent the MDC distribution and how that distribution relates to both the critical level and "true" zero. Another way to describe the MDC (when the Type II error (β) is set to 5%) is as follows:

The smallest *a priori* radionuclide concentration for which there is:

- 5% probability of obtaining a result below the critical level (i.e., 5% probability of falsely concluding that the result represents a blank);

— *and simultaneously* —

- 95% probability of obtaining a result greater than the critical value (i.e., 95% probability of concluding that there is activity in the sample and it is not a blank).

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[39] See Reference 11

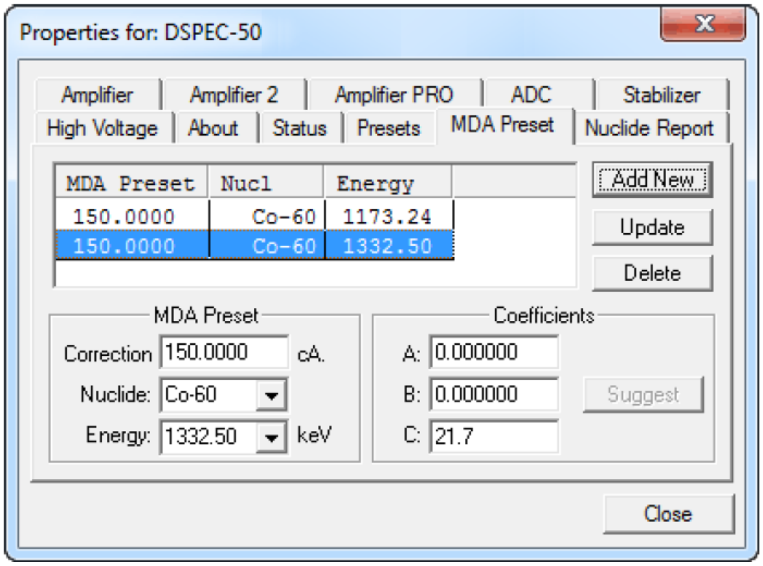
[40] See Reference 8.

Minimum Detectable Activity (MDA)

A general formula[40] for the minimum detectable activity is shown in Equation 17.

$$\text{MDA} = \frac{\text{A}+\sqrt{\text{B}+\text{C}\times\text{counts}}}{\text{Live time}\times(\text{efficiency}\times\text{yield})} \qquad (17)$$

The units for the MDA from this equation are in Becquerels/(unit sample). This is specifically different than other detection equations in that it does not perform a calculation per unit mass or volume, but per sample regardless of size. This detection formula is used in those instances where only the total activity present is of concern as for a swipe or perhaps an air particulate filter. In this formula, the constants A, B, and C are selected by the user from the available software settings a snapshot of which is seen in Figure 21. The first two constants A and B represent the user's ability to add background counts if the background about the region of interest (ROI) is zero. This prevents calculating a zero uncertainty. The value of C, often selected as 21.7 is statistically derived from the tolerable error rate of $Z_{1\text{-}\alpha}^2$ from the critical concentration formula at 5% tolerable error rate (see MARLAP for a detailed discussion of this factor).



MDA Preset	Nucl	Energy
150.0000	Co-60	1173.24
150.0000	Co-60	1332.50

MDA Preset
Correction 150.0000 cA.
Nuclide: Co-60
Energy: 1332.50 keV

Coefficients
A: 0.000000
B: 0.000000
C: 21.7

Figure 21. Screen Shots from Software Identifying Selectable Constants for MDA Equation

When the values for constants are set at A=0, B=0, and C=21.7, the formula will yield the same results as that presented below for the LLD equation (with the exception that the units for the sample are omitted).

Lower Limit of Detection (LLD)

While there are several definitions for LLD the one that is used by the Nuclear Regulatory Commission and defined in both Regulatory Guide 4.14[41] and NUREG-1301 (Reference 9) is

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[41] See Reference 10

$$\text{LLD, } \mu\text{Ci/mL} = \frac{4.66 \times \sigma_b}{(3.7 \times 10^4 \times E \times V \times Y \times e^{-\lambda \Delta t})} \tag{18}$$

Where:

σ_b = standard deviation of the background, dps
E = detector efficiency at the specified gamma-ray energy
V = volume of sample in mL
Y = Chemical yield (=1 for gamma spec)
Δt = elapsed time between sampling and counting

This equation determines an *a priori* limit of detection based on optimal characteristics of the detection system and the sample. The two most significant factors in this equation that are subject to change from the *a priori* measurement to the actual sample analysis are the value of σ_b and Δt. The determination of background is made by counting a sample container filled with the same material as a sample and with the same geometry[42], but completely void of radioactive materials. This measurement assumes that the background is constant regardless of the presence of other radionuclides in a sample. However, this is not necessarily true as the presence of other radionuclides can elevate a sample background in certain regions of the gamma-ray spectrum due to Compton and other beta decay effects that produce photons. Thus the LLD can provide an estimate of the detection limit under ideal conditions where the sample and blank background are the same.

The time between sampling and analysis brings into play the factor that if the radionuclide has a short half-life and you have counted the sample too long after sampling so that the radionuclide is undetectable then decay correction for an LLD at the time of sampling is useless.

Table 5 shows the values calculated from the different detection equations noted above. The parameters for determination of ^{137}Cs concentration, sample volume (1 L was used), count time, detector efficiency, and sample background are kept constant for each detection equation calculation on each row of the table.

When selecting an equation and constants to use for detection, the analyst should always ensure that the end user or data user (client) is in agreement with the equations and values used and that they properly accommodate the data and measurement quality objectives of the project.

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[42] Required in NUREG 1301, “Offsite Dose Calculation Manual Guidance: Standard Radiological Effluent Controls for Pressurized Water Reactors” and in ASTM D7282 (Reference 15)

Table 5. Detection Equation Calculations

			Activity at Beginning of Count Interval, pCi/L			
	Bg, cps	Detector Efficiency (at 661 keV)	Lc	MDA	LLD	MDC
21600 sec	0.01	0.01	5.0	8.6	10.1	10.5
(6 Hours)	0.05	0.01	11.3	19.2	22.5	22.9
	0.1	0.01	15.9	27.2	31.8	32.2
	1	0.11	4.6	7.8	9.2	9.2
	10	0.21	7.6	12.9	15.2	15.2
	100	0.31	16.2	27.7	32.5	32.4
3600 sec	0.01	0.01	12.3	21.0	24.7	27.0
(1 Hour)	0.05	0.01	27.6	47.0	55.2	57.5
	0.1	0.01	39.0	66.5	78.0	80.3
	1	0.11	11.2	19.1	22.4	22.6
	10	0.21	18.6	31.7	37.1	37.2
	100	0.31	39.8	67.9	79.6	79.5

Note that the value for the constants in the MDA equation used were A=0, B=0, and C=5.43. This was done to allow the numerator to align with the L_D value of twice the L_C.

Uncertainty Determination

The values reported for the analyses of samples by gamma-ray spectrometry are of little value without the associated measurement uncertainties of the results. MQO's associated with the analyses should specify the required method uncertainties for analytical results. Calculation of uncertainties can be very complex and are covered in significant detail in MARLAP (Reference 7) and GUM (Guide to Uncertainty Measurements-Reference 17). Presented here is a basic outline of the calculation process and the inputs that should be considered.

The basic process for evaluating and reporting the combined standard uncertainty (also referred to as total propagated uncertainty) of a measurement requires:

1. Identifying the measurand, Y, and all input quantities, Xi, for the mathematical model used to calculate the result. Include all quantities whose variability or uncertainty could have a potentially significant effect on the result (uncertainties <0.1% are not significant).
2. Express the mathematical relationship, $Y = f(x_1, x_2, \ldots x_n)$ between the measurand and the input quantities. In most cases for radionuclide analysis, the model will be based on the equation used to calculate the activity concentration.
3. Determine an estimate of the value of each input quantity, xi
4. Evaluate the standard uncertainty, $u(x_i)$, for each input estimate, xi, using either a Type A or Type B method of evaluation

5. Evaluate the covariances, $u(x_i, x_j)$, for all pairs of input estimates with potentially significant correlations (this is occasionally difficult to evaluate and is often ignored since it is usually small compared to other uncertainties.

The combined uncertainty can then be calculated using guidance in MARLAP (Chapter 18). Alternatives for calculating combined uncertainty include commercial computer programs and free programs that follow GUM principles. These include GUMCALC available at http://www.mccroan.com/gumcalc.html and others that can be obtained by searching the web. These programs allow the user to develop a model for calculations and input variables to be included in uncertainty calculations.

While the most convenient method for the uncertainty of activity concentrations is the software that is used for analysis of the gamma spectrometry data, this only uses input parameters that are specified in the equations in the software. Usually, the uncertainties of input parameters included are:

- Peak background
- Peak area
- Gamma-ray abundance
- Efficiency at the specific gamma-ray energy

User input includes providing uncertainties for nuclear data including uncertainties for branching ratios, uncertainties for half-lives or decay constants. The software also will calculate the uncertainties associated with decay corrections to the start or midpoint of the count interval, and from the start of the count interval to the sample collection time. There is usually an option for user-defined uncertainties that have been evaluated such as uncertainties associated with sample positioning. This option is usually available in more sophisticated software packages.

Other sources of uncertainty that may need to be considered, but may not be included in the gamma spectrometry software, are:

- Use of an aliquant versus the entire sample
- Density difference between standard and sample
- Sample inhomogeneity
- Mass or volumetric measurements

It is recommended that the user carefully review the source code to validate the methodology used to calculate the combined standard uncertainty.

J. Detector Calibration and Non-Routine Counting Geometries

Energy and Resolution Calibration

The process of instrument set-up includes assuring that proper electrical capacity and voltage regulation/surge protection have been installed, the detector shielding is securely in place, several calibration geometries have been selected, the detector has had sufficient time at liquid nitrogen temperature to ensure that it is at equilibrium, and the manufacturer's voltage for that detector has been applied. Once the manufacturer's method for this set up has been completed, the next step is energy calibration. The user must decide the number of channels that will be used for the energy range of gamma-ray emitters of interest. That number of channels usually spans 59 to 1836 keV (the energies of the routine low and high energy calibration sources). In most cases the energy calibration used will be approximately one of the following three:

- 1 keV/channel
- 0.5 keV/channel
- 0.25 keV/channel

A radioactive source is obtained that contains radionuclides that emit gamma rays at energies that span the energies expected in samples to be analyzed.

The source used should be of sufficient strength so that the uncertainty of the net counts in each gamma-ray peak contributes negligibly to the combined standard uncertainty. Guidance provided in ANSI 42.14[43] discusses using 20,000 net counts and 50,000 net counts for the efficiency and shape calibration functions, respectively. These net counts should be achieved in a reasonably short period of time so that any variability in detector environmental conditions is also minimized.

The source is counted and the channel numbers of each photopeaks' centroids are plotted against the known energy of those peaks and the slope of the curve calculated. The gain on the amplifier may be adjusted and the standard recounted. This process is repeated until the peaks are in the channel desired to fit the energy calibration. The source is recounted so that sufficient counts in each of the peak centroid channels are accumulated and a calibration for energy and resolution can be calculated by the software. Energy calibration over the range of 59 to 1836 keV is quite linear. Beyond those limits, the energy may stray from perfect linearity. Energy calibration (E) as a function of channel number x is shown in Equation 19 (a commonly used formula for energy calibration):

$$E = C_0 + C_1 x + C_2 x^2 + C_3 x^3 \tag{19}$$

Where:

C_0, C_1, C_2, and C_3 are coefficients determined by the calculation performed by the software

E is the photopeak energy in units of keV

x is the channel number of the centroid

This equation is a typical approach to energy calibration and assumes a cubic fit of the data. Other equations for energy calibration may be available in the software.

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[43] See Reference 16

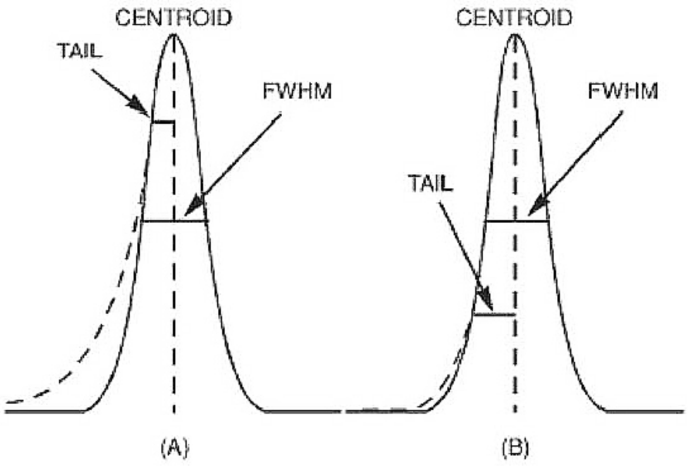

Figure 22. Calibration for Resolution

The term resolution refers to the full-width-at-half-maximum (FWHM) of a photopeak. The FWHM is determined by taking the number of net counts in the peak centroid and dividing by two. The channels that correspond to these counts on either side of the photopeak energy are converted to energy and difference between these two energies is the FWHM.

One method for calibration of resolution uses peaks like those shown in Figure 22 which are fitted to a modified Gaussian curve and assumes that the FWHM = 2.355xσ, where σ is the standard deviation for the modified Gaussian curve[44]. The peak centroid is determined from the data points and may not be one of the actual data points since the curve is fitted to the Gaussian shape.

A FWHM calibration curve is generally constructed using data collected during the energy calibration. The observed FWHM is plotted as a function of energy (or channel). A commonly used formula for resolution calibration is

$$\text{FWHM} = \frac{F_0 + F_1\sqrt{E}}{C_1} \qquad (20)$$

Where:

E is the gamma-ray energy in keV,
C_1 is the "gain" term from Equation 19, and
F_1 and F_0 are the coefficients of the FWHM equation

The coefficients for equation parameters (e.g., F_1, C_1, etc.) are empirically determined for each detector based on the response of the instrument.

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[44] See Reference 21

Efficiency Calibration

It is of paramount importance that the physical geometry of the sample is identical to that of the standard used to calibrate the detector. In addition, the juxtaposition of the sample container with respect to the detector must also match the standard container position when the standard was used to calibrate the detector. Figure 23 is an example of an HPGe efficiency calibration curve. It displays the energy dependence of the efficiency for one particular sample container in a specific sample container to detector configuration.

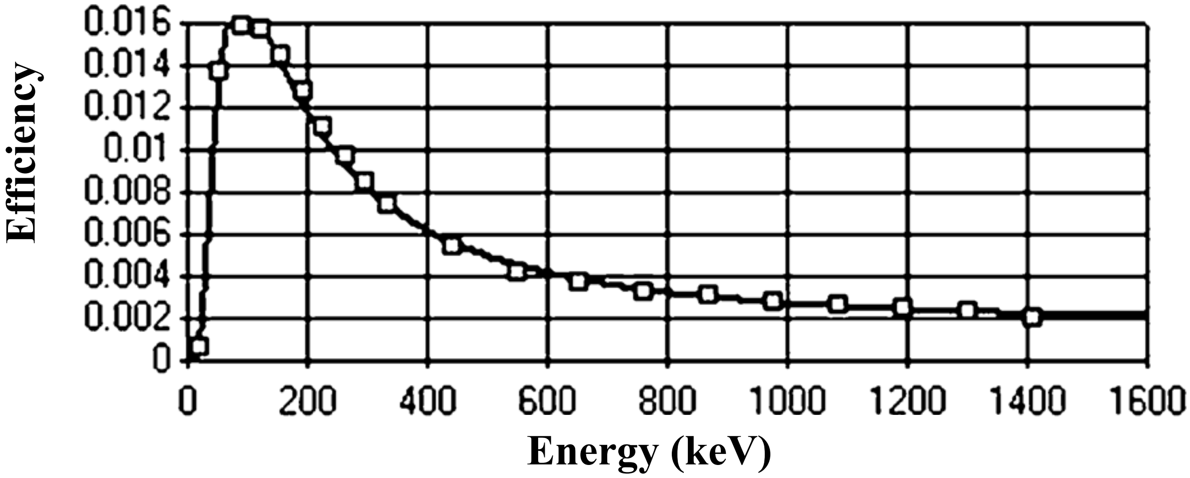

Figure 23. Example of an HPGe Efficiency Calibration Curve

The parameters that affect the ability of this calibration curve to accurately determine the activity concentration in a sample are:

- The height to which the sample container is filled;
- The density and chemical composition of the sample matrix;
- The physical composition of the sample container; and
- The thickness of the sample container,

when these parameters are compared to the working calibration source (WCS).

Once the analysis of the working calibration source (WCS) has been completed, the peak areas for each of the gamma rays to be used for determining efficiency are compared to the gamma activity of the WCS, as stated on the certificate received from the WCS manufacturer, using the following equation:

$$\varepsilon = \frac{N_S/t_S}{A_D} \quad (21)$$

Where:

ε is the efficiency for the gamma-ray peak of interest
N_S are the net counts in the gamma-ray peak of interest
t_s is the WCS count time

A_D is the certified activity at the gamma-ray peak of interest, gammas/second[45]

Once all the efficiencies for the gamma rays selected for use in the detector calibration are calculated, a curve is fitted to the data using one of the model equations in the software that is selected by the user. It is important to review the shape of the curve and to assess the fit of measured points to the curve to ensure it will be suitable for use. The importance of this is shown by the following two figures. In Figure 24 a fourth-degree polynomial was selected to create the calibration curve. While the overall shape of the curve parallels the response of germanium for gamma rays, note especially that two of the points fall rather far below the smoothed curve. This is particularly bad since it is in the region of the “knee” where the curve reaches a maximum and the slope changes dramatically from positive to negative. In Figure 25 the same measured data was fitted to a fifth order polynomial. In this case, the model equation used for fitting the curve produces a smooth curve that parallels the response of germanium for gamma rays and all of the points lie very close to the calibration curve. It is recommended that documented criteria for acceptance of calibrations be defined in advance to ensure that the fitted curves adequately reflect measured efficiencies. One approach that has been used is to establish a limit to the acceptable deviation between measured and fitted values for each point in a curve.[46]

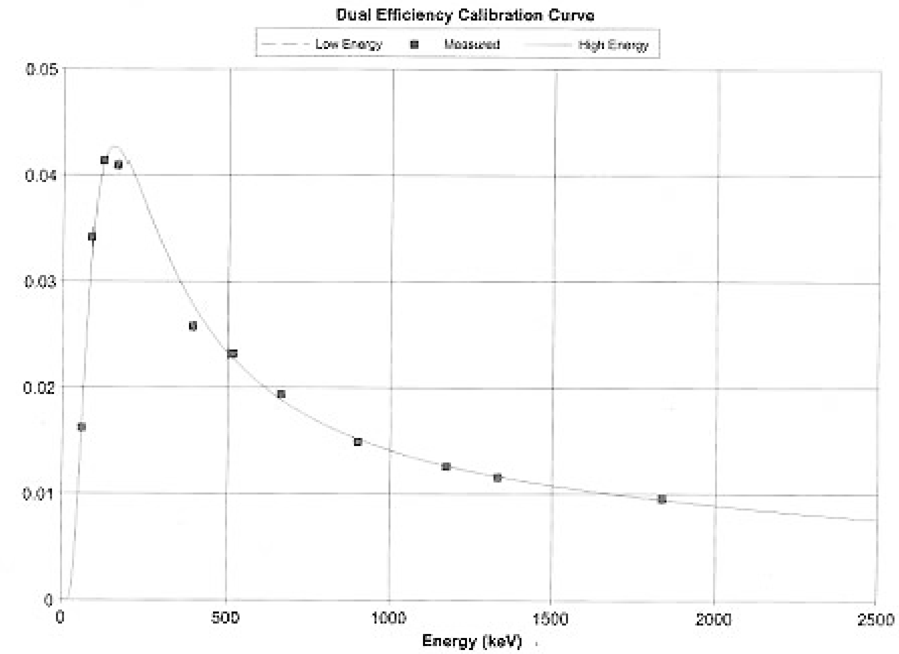

Figure 24. Fourth Order Calibration Curve

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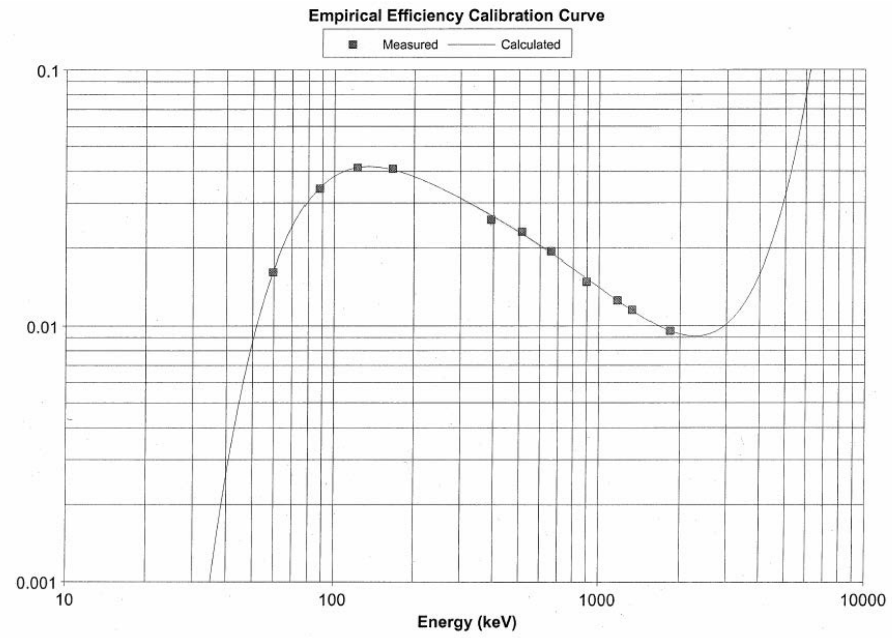
[45] Note the units for the activity of the WCS are gammas per second and not dps, curies or another derived unit. Thus the numbers of gamma rays interacting via the Photoelectric Effect are compared directly to the number of gamma rays emitted by the WCS.

[46] ASTM D7282, *Standard Practice for Set-up, Calibration, and Quality Control of Instruments Used for Radioactivity Measurements*, describes such an approach (Reference 15).

Figure 25 demonstrates that even when an acceptable curve is obtained by fitting measured points, it is important not to use the efficiency calibration curve beyond the bounds of measured points. In this case, the curve takes a dramatic upswing in efficiency after the final calibration point, which does not reflect the physical response observed in an HPGe detector.



Datasource: DET08_8K
ln(Eff) = -4.217e+000 + 7.494e-001*x - 1.859e-002*x^2 - 1.486e-001*x^3
+ 1.225e-001*x^4 - 3.619e-002*x^5
where: x = ln(9.478e+002/E)

Figure 25. Fifth Order Calibration Curve

Once the user is assured that the data produced by counting the WCS have produced a curve that is satisfactory, the efficiency curve is verified to be correct with an independent source of known activity. When this also produces results for each gamma-ray emitter in the second source that is deemed acceptable, the calibration is complete. The user should determine acceptability using a statistical model based on the uncertainty of both measurements (e.g., the Z-score).

K. Correcting Efficiency for Matrix/Geometry Differences

The sample container, the size of the sample (the fill-volume of the sample in the container), the sample density, and the sample composition all have an impact on interactions of gamma rays that will affect the number of gamma rays that reach the detector. The size of the sample container, the sample and its fill volume in the container may lead to differences in attenuation. These factors can be controlled by the laboratory staff by ensuring that samples are only prepared and counted in geometries which closely match that of the calibration standards used for the analysis.

Figure 26 shows efficiency curves for four different food-related matrices analyzed on the same detector in the same container, sample size and juxtaposition to the detector, but for which the density and the composition of the sample varies. The differences in efficiency observed, especially at lower energies, are greater than thirty percent. These are attributable to differences in self-attenuation associated with the density and to a somewhat lesser extent, the composition, of samples.

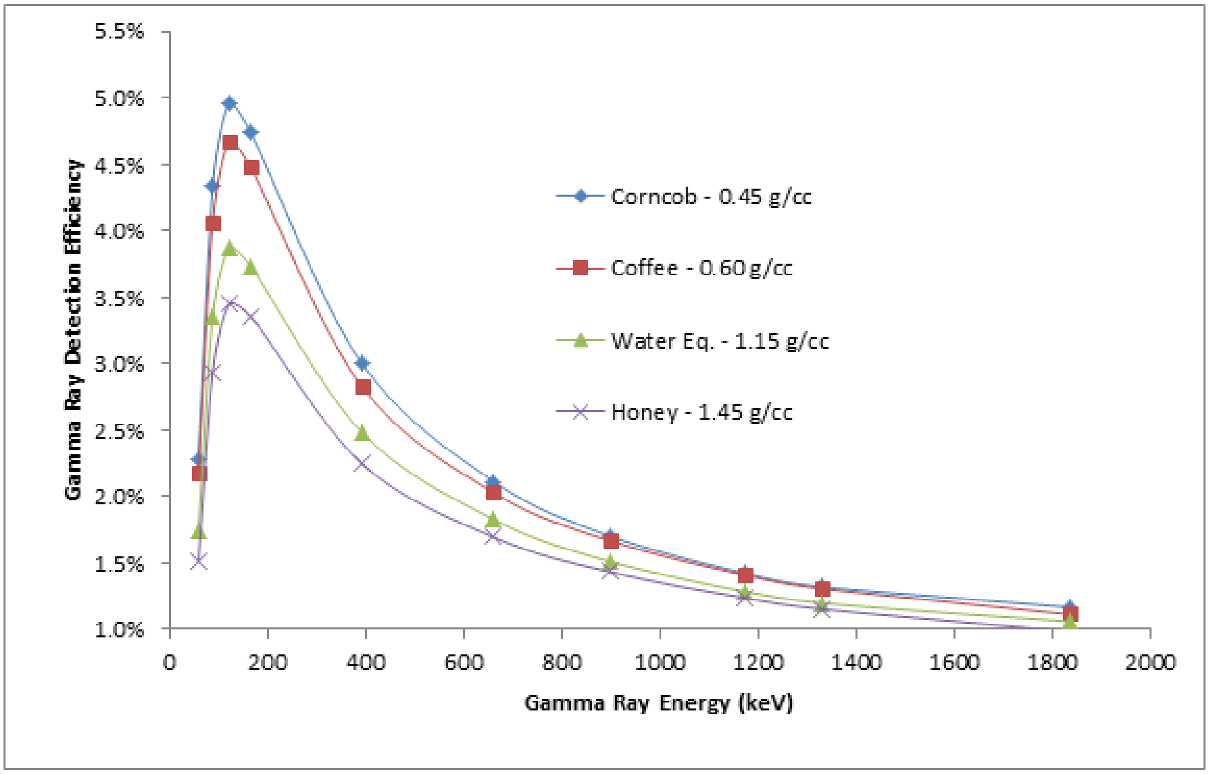


Figure 26. HPGe Detector Efficiency Curves for Four Solids

Empirical Corrections for Attenuation

The best method for calibrating detectors in a radiochemistry laboratory involves the use of physical standards containing radionuclides (traceable to a National Metrological Institute such as NIST in the United States) in a geometry that exactly matches that of the samples. When differences in the size, density, and composition of samples being measured result in a large and significant difference in detector efficiency, the detector should be calibrated using a calibration standard matrix that exactly matches the levels, geometry, and levels of attenuation in the samples being analyzed.

The traceability and reliability of measurements are one of the more important reasons to rely on fixed laboratories. In contrast to field measurements, where mathematical approaches to efficiency calibration may represent the only viable approach for performing measurements, the fixed laboratory can more easily control different aspects of the measurement situation. The laboratory can homogenize samples, place them in the same container using the same fill-volume, and count them in a very tightly controlled juxtaposition to the detector. It can identify and isolate between samples of different density and matrices. Finally, and most importantly, it can obtain traceable standards in various containers, matrices, and densities and calibrate in configurations that match those most commonly used for samples. However, economic and operational factors will limit the number of configurations that a lab can afford to maintain.

Mathematical, Modeled, and other Corrections for Efficiency and Attenuation

While empirically-based calibrations allow laboratories to obtain results that are defensible and relatively accurate, it may be possible to improve the quality of results by generating and applying correction factors to account and correct for minor differences between sample geometries and the calibration standards. Two factors generally are outside of the control of the laboratory, the density and matrix composition (i.e., average Z) of the samples, are the most likely of these.

A number of approaches, some of which are integrated into gamma spectrometry software packages, are available to accomplish this. These range from Monte-Carlo simulations with well-characterized detectors and geometries, to manual or spreadsheet-based calculations to correct for differences in attenuation due to density. In general, the corrections being applied should be relatively small and should be minimally related to the skill and experience of the analyst. It would not be advisable to rely on software to extrapolate efficiencies for a Marinelli beaker geometry starting with a point-source geometry for the characterization of the detector since this requires substantial skill for determining the relationship between the two geometries (e.g., to build a model of a Marinelli beaker).

No matter what approach is used, it is important to ensure that the method/approach has been validated using traceable standards that span or bracket the range of the corrections being applied. The method should include an approach for estimating the measurement uncertainty and the approach should consistently improve the accuracy of measurement results (i.e., combined bias and uncertainty). Finally, it is important that quality control samples be used to show that the performance of the approach is reliable and consistent with the documented results of the method validation under the conditions applied.

L. Establishing sample/matrix specific libraries in the software

The main library that is often supplied with the original software package has hundreds of radionuclides and their nuclear constants listed. However, using such a large library to analyze each sample can prove to be counterproductive to obtaining a correct analysis of the sample as many of the radionuclides cannot possibly be in that sample. A specific example is a sample taken which contains fresh fission products. There are many radionuclides from the left side of the Line of Stability[47] that could not possibly be in the sample, yet they are listed in the main library. It should be emphasized here again that the library should reflect the nuclides that would be expected in the type of sample being analyzed.

Laboratory staff should be aware of the source (origin) of the sample and which gamma emitting radionuclides are likely to be present. The library used for the analysis should consider the following data regarding the sample:

- The specific matrix.

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[47] Radionuclides on the left of the Line of Stability are neutron deficient; fission products are neutron rich. See www.nndc.bnl.gov/chart

- The potential list of radionuclides that can be present based on the event.
- The half-lives of the potential radionuclides with respect to the age of the sample.
- Specific requirements of the software package (e.g., peaks needed to resolve interferences).

Once these parameters are identified, the potential list of radionuclides to be included in the sample-specific library will be minimized. Additionally, when short-lived radionuclides may be present, it may be necessary to create a different library for different sample ages. A specific example provides some of the thought processes that would go into such a sample specific library.

Example:

> A batch of air particulate and charcoal cartridge samples from a nuclear power plant that had an atmospheric release about 5 days ago has been received by your laboratory. The plant was in full operational mode and a spill of several hundred gallons of reactor coolant occurred when the ventilation filtration was out of service. The air particulate filter precedes the charcoal cartridge in the air flow. About $4.1x10^7$ cm^3 of air sample was passed through the collection device. The time period from sampling to the laboratory is one day. Sample analysis turn-around time is to be one day.

The sample matrices are air particulate filter and charcoal cartridge. Each matrix should have separate libraries since the physical forms of radionuclides that can be collected on each will be different.

Table 6. Potential Radionuclides on Charcoal Cartridge

Radionuclide	^{88}Kr	^{85m}Kr	^{85}Kr	^{88}Rb			
"True" Half-life	2.84 h	4.48 h	10.8 y	17.8 min			
Radionuclide	^{135}Xe	^{133m}Xe	^{133}Xe	^{131m}Xe	^{133}I	^{131}I	**^{129}I**
"True" Half-life	9.14 h	2.20 d	5.25 d	11.8 d	20.8 h	8.03 d	**$1.57x10^7$ y**

Table 7. Potential Radionuclides on Air Particulate Filter

Radionuclide	^{88}Rb	^{86}Rb	^{91}Sr	^{91}Y	^{92}Sr			
"True" Half-life	17.8 min	18.6 d	9.63 h	58.5 d	2.66 h			
Radionuclide	^{92}Y	^{137}Cs	^{140}Ba	^{140}La	^{141}La	^{141}Ce	^{143}Ce	^{144}Ce
"True" Half-life	3.54 h	30.1 y	12.8 d	1.68 d	3.92 h	32.5 d	33.0 d	285 d

The primary consideration for the list of radionuclides for this type of incident is that they would be volatile fission or activation products. Tables 6 and 7 contain the most likely candidates for the library based on volatility, parent-progeny relationship, and half-lives greater than two hours (less than two hours it becomes extremely unlikely that they would be observed since the radionuclides would have undergone 72, 2-hour half-lives). Kr-88 and its progeny ^{88}Rb are eliminated (grey boxes) since they too would have gone through significant decay during that time period. I-129 is eliminated (cross-hatched box) due to its extremely long half-life (an insignificant number of counts would be realized in the short time available to analyze the samples). Because there is a large volume of air collected it is likely that there will also be some naturally-occurring radionuclides in this sample such as ^{212}Pb, ^{212}Bi, ^{214}Pb, ^{214}Bi, ^{7}Be, and ^{208}Tl; all of which could be seen in both samples.

The next step would be to decide how many gamma-ray energies for each radionuclide need to be included in the library. The main library will usually have all gamma-ray energies down to about 1% abundance included. Consideration should be made for potentially using energies that are down to 0.1% for this specific library.

The half-lives of progeny should be evaluated based on the timing of the sample following the event. Specifically, ^{140}Ba/^{140}La which may be in Transient Equilibrium should be carefully examined when decay correcting to sample data/time from the beginning of the count. All other radionuclides present in the tables are in the No Equilibrium situation and their "true" half-lives can be used.

Once the samples have been counted it is imperative that a thorough review of any unidentified lines be performed to ensure that the basic assumptions regarding the release are correct (e.g., volatile fission or activation products and their progeny).

Creating a library that is specific for an event or specific to a sample type (and not using the master library) is an extremely important step in minimizing incorrect identifications and quantifications.

M. Gamma spectrometry report review processes (verification)

The analysis of a sample by gamma spectrometry yields a report containing activity results based on the input parameters that were selected by the analyst. The data review process should ensure that not only are the usual editorial inputs correct (i.e., date/time of the sample, date/time of count, correct detector, correct library, etc.) but that the results for all of the reported radionuclides make sense. The review should also consider:

- Sample related data are correct.
    - Correct sample size entered.
    - Correct density used.
- Impact on the results of the following selected preset software configurations.
    - Correct calibrations used.
    - Correct peak background subtraction used (if any).
    - Correct summing and attenuation corrections used.
    - Half-life ratio function value.
    - Allowable energy difference between identified peaks and library values.
    - Abundance limit selected (if used at all).
    - Weighted mean average calculation.
    - Correct date for decay correction used.
    - Decay correction to start of the *count* interval.
    - Decay correction to the end or midpoint of the *sampling* interval.
- Peak Search and Identification.
    - The FWHM of all peaks used in the analyses are reasonable for the energy range that the peaks were found.

  - Deconvoluted peaks do not negatively impact quantification.
  - Peak flags investigated including visual inspection of the spectrum.
  - More than one radionuclide activity concentration *is not* calculated using the same data from the same gamma-ray peak also ascribed to another radionuclide.
- Library.
  - Correct library used – if a different library was used, rationale for change documented.
  - Library correctly accounts for potential parent-progeny relationships.
  - If the library was modified, changes made are documented and validated by a cognizant reviewer prior to final reporting of results.
- Nuclide Identification and Quantification.
  - Presence of a radionuclide is detected but not one that is closely associated with it (e.g., ^{95}Nb is detected but not ^{95}Zr).
  - Calculated, individual gamma-ray activities are in the appropriate ratios based on the abundance of those gamma rays and the efficiency of the detector at their energies.
  - Presence of unexpected radionuclides is investigated.
- Measurement quality objectives meet the clients' specifications/needs (or laboratory defaults if none from the client).
  - Critical level concentration or minimum detectable concentration.
  - Method uncertainty requirements were met for each radionuclide.
  - Results for requested radionuclides have been reported.
- Data Reporting.
  - Results and uncertainty and units reported for all required radionuclides (and any other parameters required by the client or laboratory default such as critical level).
  - Actual values reported (not results such as "zero", "<MDC", or "ND").
  - Decay correction date reported together with results.
  - Do any results data require a qualifier?
- Documentation.
- All information necessary to reproduce the results found in the report.
- Event that created the radionuclides in the sample.
- The type of sample matrix.

This is a long list of issues to be addressed by the person performing the data review process. A method of helping to ensure that there is complete attention to all these details is to provide the data reviewers with a procedure or a checklist. An abbreviated example of such a checklist is shown in Table 8.

Table 8. Checklist (partial) for Gamma Spectrometry Data Verification

Sample Matrix_______	Sample Date/time___________	Sample ID_________
Geometry__________	Detector_______	Count date/time_____
	Y	N
• Are all of the above inputs identified correctly in the report?	__	__
• Are all identified radionuclides included based on half-life?	__	__
• Have appropriate members of decay chains been identified?	__	__
• Are proper half-lives used for radionuclides in parent-progeny relationships?	__	__
• Are all the FWHM used to calculate activity concentrations at the approximate value of the gamma-ray energy?	__	__
• Are all identified radionuclides expected or probable?		
• Was the correct library used?	__	__
• …	__	__
• Any "N" requires a description and resolution	__	__

The exact nature of the questions for this form are to be decided by the individual laboratory staff in cooperation with the client, but clearly when any of the noted issues does not meet expectations a description of why this occurred and how it may need to be resolved should be part of the review process.

N. Data validation and reporting protocols

Data should always be validated before they are deemed acceptable for decision making. The validation process will go through the entire sample history including the sampling process, preservation, and storage as well as the parameters used to analyze the samples. All of these are important in gamma spectrometry as the assumptions made about parent-progeny relationships and decay correction will all be tied into these actions. An example of a data validation guide is shown in Table 9.

Table 9. Example Data Validation Table

Project: ___________	Client: ______________
Project QA Document:________	Analytical Laboratory Used: _____________
Are the following satisfactory:	
Sample COC?	Y___ N___
Sample Preservation?	Y___ N___
Sample holding time?	Y___ N___
For any “N” provide explanation: ____ ____	
All verification report inputs satisfactory?	Y___ N___
If “N” provide explanation: ____ ____	
All QC analyses Satisfactory?	Y___ N___
For any “N” provide explanation: ____ ____	
Have all software preset functions been optimized based on the client requirements and sample history to identify the radionuclides present?	Y___ N___
Client Requirements Met?	Y___ N___
Sensitivity Factor:	
Half-life ratio:	
Energy Difference:	
Abundance factor:	
Key line:	
Weighted Mean:	
Have all unknown gamma-ray lines with a cps 1-sigma uncertainty less than 50% been identified?___	Y___ N___
List all unidentified gamma rays: ____ ____	

Quality system requirements generally specify two levels of validation: one from a technician and one from a manager. Most software packages provide this option. Each facility should procedurally establish expected criteria for software and analytical validation (electronic or otherwise). This is another laboratory protocol that should be stated in the radiochemistry Quality Manual.

O. References

Documents

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Consensus Standards

Some recognized standards (i.e., published by a standards organization either nationally or internationally) and some published in the refereed literature for the analysis of radionuclides in soil, are included below. The American Society for Testing and Materials (ASTM) methods may be purchased online from www.astm.org. However, in every case, the individual laboratory must perform method validation in their own laboratory for a soils matrix to ensure that the results will conform to the needs of the incident.

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ATTACHMENT I: INSTRUCTIONS TO LABORATORIES ANALYSIS OF FRESH MIXED FISSION PRODUCT PROFICIENCY TEST SAMPLES ROUND III - DECEMBER 2012

I. Introduction

EMS, as a contractor to the U.S. Environmental Protection Agency, is providing your laboratory with the third in a series of irradiated uranium proficiency testing (PT) samples as a simulation of the type of environmental water sample that might be encountered following a fission event (e.g., an improvised nuclear device (IND) or reactor accident event). The mission of this program is to provide laboratories with an opportunity to analyze samples that contain a complex mixture of radionuclides that are representative of what might occur following a fission event. This objective of the study is for these PT samples to allow laboratories to identify areas of strength and improvement in their analyses and reporting of such complex radioanalytical samples.

II. PT Sample Description

The sample you will receive directly from our supplier[48] will contain fission and activation products resulting from a one-hour neutron irradiation of uranium oxide (U_3O_8). The oxide will have undergone irradiation in early November 2012. The PT provider will prepare a stock solution by dissolving the oxide in nitric acid. The solution will be stabilized with an iodate carrier. Within several weeks of the irradiation, you will receive a proficiency test (PT) sample of diluted stock solution.

The reference date (i.e., sample collection date) for decay correction purposes, as well as the irradiation date (i.e., date of the "event"), will be sent to participating laboratories by EMS **PRIOR** to the laboratories receiving the samples.

The sample is assumed to be surface water from an estuary that has been affected by the event. The reference date (i.e., sample collection date) will be at least two weeks after the irradiation of the oxide.

The activity will be significantly greater than environmental sample matrices that are normally encountered *but will not exceed 0.1 microcuries (0.1 µCi) total activity*. The PT provider will verify prior to shipment that the level of radioactivity in the samples is consistent with inventory restrictions established under each facility's radioactivity materials license (or the equivalent inventory restriction at DOE facilities). The sample will also contain fission products that are not gamma emitters such as ^{90}Sr and $^{239+240}$Pu (in sub-nanogram quantities), and sub-milligram quantities of uranium isotopes. The concentrations of these non-gamma emitting radionuclides that will be used as "accepted values" for general comparisons will be calculated from mathematical models.

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[48] Eckert & Ziegler Analytics, 1380 Seaboard Industrial Boulevard, Atlanta, GA 30318. Samples will be shipped overnight express on or about December 5, 2012; you will receive advance notice of the actual shipping date.

III. Sample Analysis Instructions

Gamma-ray spectrometry analysis is requested of all study participants. Additionally, the determination of ^{90}Sr, ^{89}Sr, and $^{239+240}$Pu activity concentrations should be performed by laboratories who maintain capabilities for these analyses. The laboratory should use the same approved processes and procedures that would be used for receipt, handling, analysis, and reporting for a similar sample during an incident response. Deviations from approved procedures that are necessary to comply with the requirements of this SOW should be documented in the case narrative.

Prior to receiving the sample, we recommend that the laboratory have a process by which summing effects can be minimized (e.g., counting samples several inches from the detector surface, or diluting the sample), and that process should be described in the case narrative.

The sample will be shipped in nitric acid solution so that the sample pH is less than 2.0. Upon receipt, the laboratory's protocol for screening samples shall be used. Reporting of the screening results (either as count rate, dose rate or activity) for the sample and its package upon receipt is a required deliverable for this study. These screening measurements should be converted into a pCi/L concentration for the sample. If the laboratory does not have a method for doing this, that should be stated in the report.

Dilution of the sample may be performed if your laboratory protocol requires dilution, and your available sample geometries provide adequate sensitivity to meet the combined standard uncertainty requirement stated below. ***Nitric acid must be used for this dilution***, maintaining a pH of less than 2.0 during the dilution process. Note that radioiodine will be carried in the solution by added stable iodate. *It is strongly recommended that the laboratories provide adequate means to ensure all radionuclides remain soluble during sub-sampling and throughout the gamma analysis counting interval. Based on the laboratory's experience, chemical additives may be an acceptable method of ensuring that all components remain soluble.*

IV. Gamma Spectrometry

The gamma spectrometry sample results should be reported based on a single count.

NOTE: This is a change from the previous studies.

- The sample count date will be specified by e-mail prior to the arrival date (within 1–2 days) of the sample.
- For each laboratory, the sample should be counted only once and the results of that count decay corrected to the "sample collection date" and reported; no averages from multiple detectors or multiple sample counts are to be reported.
- The laboratory is to count the sample for gamma spectrometry analysis so that relative combined standard uncertainty (1-sigma CSU, i.e., k=1) for ^{147}Nd is less than or equal to 13%. *The count time may be adjusted and the count repeated to achieve this value.* Please note that it is not intended to limit the count time for the sample.
- Upon achieving the relative CSU specification for ^{147}Nd, all radionuclides in the sample which have less than 50% counting uncertainty (1-sigma, k=1), and are considered "detects" (no "U" qualifier) should be identified, and the measured activity and associated combined standard uncertainty (1-sigma, k =1) shall be reported.

  - It is understood that all peaks with > 50% counting uncertainty may not be used in the quantification of the radionuclide of interest. For peaks that are not used in the quantification of a radionuclide that is otherwise being reported, the raw data should be annotated or the report or case narrative should correctly attribute the peak to the source radionuclide(s) of interest.
- In cases where specific radionuclide concentrations are present due to parent or progeny activity but may be indirectly determined from gamma spectrometry results, the indirect radionuclide activity concentration and combined standard uncertainty should be reported. Assumptions of equilibrium (e.g. secular, transient, etc.) should be noted in the report or the case narrative.
- Non-routine activity calculations, such as those addressing non-equilibrium ingrowth factors, which are not performed by the gamma spectrometry software, should be included in a separate Excel spreadsheet or other document attached to the report.

The reference date (i.e., sample collection date) for this sample and the irradiation date (i.e., the date of the "event") will be sent to participating laboratories by EMS **prior** to the laboratories receiving the samples. *NOTE: The method of decay correction to the sample date for some radionuclides may require a method not commonly used by the laboratory's gamma spectrometry software.*

V. Reporting Requirements

Two documents are necessary to evaluate the laboratory's data and information. EMS requires only emailed files: paper copies are neither required nor desired.

Document 1. The following information shall be included in an Excel spreadsheet (to be provided by EMS upon confirmation of your participation in this study) for the gamma spectrometry, radiostrontium, and plutonium analyses measurements.

Do not modify the format of the spreadsheet or add any other information besides:

- The Laboratory Name (as specified on the shipping papers for the source to the laboratory), and sample identification.
- Final analytical results and combined standard uncertainty (1-sigma, k = 1) for each radionuclide identified on the *lines dedicated for each radionuclide* in the top section of the worksheet.
- The activity reference date (i.e., the "sample collection date") has been filled in. Please do not alter this date. Fill in the date /time of the count for each of the different analyses performed. For radiostrontium, analysis use the first count date/time if two are used.
- Any *gamma spectrometry* result that the laboratory would qualify as a "non-detect" (e.g., a "U" qualifier) *should not* be included on the spreadsheet, even if space is provided for that analysis.
- The bottom section of the worksheet will be for those detected radionuclides that are not listed on the top section. Fill in the radionuclide identity and, again please include only the data for those radionuclides that would be considered a "detect".

Results from screening data *should not be included* in the Excel worksheet.

Document 2. A more detailed document should be used to transmit the final analytical results and the requirements identified in this document for each analysis, respectively (a single pdf file that combines all the submitted information is preferred).

The results of the gamma spectrometry analysis should be e-mailed to EMS within one week of the analysis date of the sample. EMS requires only an e-mailed pdf file: paper copies are neither required nor desired.

The analytical values for the gamma spectrometry measurements shall be reported with the following information:

1. A summary report of the final activity concentration and the associated combined standard uncertainty (coverage factor $k = 1$) for each radionuclide identified in the sample, in pCi/L, using appropriate rounding methods, decay corrected to the date on the documentation received from the PT sample supplier (the reference date).
2. A description of any sample pre-treatment performed, including additional preservation, filtration, or steps taken in the laboratory to ensure quantitative transfers from the original container or representative sub-samples for the individual analyses.
3. Volume of sample counted for each of the analyses. Dilution process if sample was diluted. The reported combined uncertainty shall reflect uncertainty from volumetric/ gravimetric dilutions.
4. Gamma spectrometry raw data printout with:
    a. Summary of all peaks located by the peak search algorithm - should include peak energy, FWHM, background activity at that peak and any qualifiers that the software uses to identify gamma rays that may not be acceptable for quantitation.
    b. Activity and CSU for each individual gamma-ray peak used in the computation of the final reported activity.
    c. A list of all gamma-ray peaks located by the software routine but not identified during analysis or review of the spectrum.
5. In addition to the information presented in the gamma spectrometry raw data printout:
    a. User selectable analysis options should either be reported in the raw data instrument printout or narrated. This should include: peak search sensitivity, half-life ratio limit, peak matching energy tolerance, background, and modifications to peak-search algorithms based on the sample activity.
    b. If any modifications to routine parameters were performed, these should be addressed in the narrative. This should include coincidence summing corrections, nuclide interference calculations, and algorithms used for parent/progeny calculations.
6. Gross activity screening results (dose or cpm and the algorithm used to convert to activity and the reference nuclide used to calibrate the screening instrument), uncertainty, units (pCi/L), instrument(s) used, and a description of any safety precautions taken as a result of the screening process.

The reports ***do not*** need to include the following information, as it is not used to analyze laboratory results:

- Calibration spectra

- Calibration certificates
- Quality control sample results (specifically *do not include* results for LCS, instrument blanks, or duplicates)
- Method blank sample results
- Instrument performance checks
- Certifications for various agencies

Please do not include any of this information with your reports.

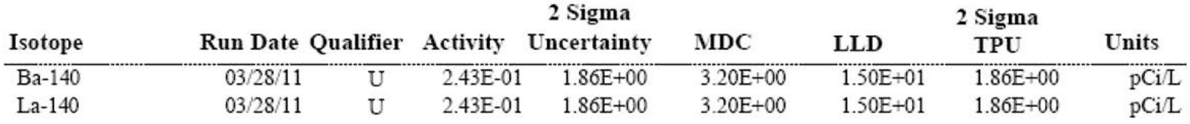
ATTACHMENT II: EXAMPLES OF RADIOANALYTICAL DATA REVIEW AND REPORTING PROBLEMS

The data presented in this attachment were taken from reports submitted for various types of samples. Each example starts with a figure. Each figure is followed by a discussion of issues that arose with the analysis which include at least some of the following:

- Half-life
- Equilibrium type
- Library assignment
- Preset analysis configuration
- Identification of energy associated with more than one radionuclide
- Sample geometry
- Detector geometry
- Preservation of the sample when it was analyzed

In all the examples presented here the issues identified have been appropriately addressed by the contributing organizations.

Example 1: Analysis of ^{140}Ba/^{140}La in Rainwater Samples- Incorrect Use of Decay Correction and Equilibrium



Isotope	Run Date	Qualifier	Activity	2 Sigma Uncertainty	MDC	LLD	2 Sigma TPU	Units
Ba-140	03/28/11	U	2.43E-01	1.86E+00	3.20E+00	1.50E+01	1.86E+00	pCi/L
La-140	03/28/11	U	2.43E-01	1.86E+00	3.20E+00	1.50E+01	1.86E+00	pCi/L

Figure 27. Incorrect Equilibrium Assumed for ^{140}Ba/^{140}La

The above results are excerpted from an analysis report on rainwater samples taken on March 23, 2011, received by the contract laboratory on March 25, 2011, and analyzed on March 28-29, 2011 following the Fukushima event (which occurred on March 11, 2011). Sample activity was to be corrected to the date of sampling. The “U” qualifier denotes that the MDC for each radionuclide was calculated, and the measured activity is less than the MDC. Ba-140 and ^{140}La form a transient equilibrium pair and assuming that there were no ^{140}La initially present and no environmental fractionation, after approximately 5 days the transient equilibrium activity ratio of ^{140}La/^{140}Ba would be 1.15. In this analysis the same gamma ray, 1596 keV, was used for the analysis of both radionuclides; it is the most abundant gamma ray for ^{140}La. A half-life of ^{140}Ba, 12.8 days, was used to decay correct the ^{140}La activity concentration back to the date of sampling. The activity concentration of the ^{140}Ba was determined inferentially by assuming secular equilibrium with the ^{140}La (based on the 1596 keV peak area).

However, the report did not take into account:

1. That Ba-140 was not measured rather an assumption of secular equilibrium with ^{140}La was made.
2. That making a decay correction for ^{140}La (decay progeny) prior to the date of collection assumes that equilibrium had been achieved during the aerosol transport across the Pacific

Ocean. Radioactive equilibrium, however, may not have been achieved at the date of sampling.

3. That the activity concentration of ^{140}La at transient equilibrium is higher than that of ^{140}Ba. Concerns listed in #1 and #2 notwithstanding, calculating parent activity based on measurement of progeny in equilibrium, would require applying the correct factor to account for the ratio of parent and progeny at equilibrium (1.15).
4. If any sample preservation was performed.
5. Using two different detection criteria (LLD and MDC) is very confusing to any reviewer. Why would two be necessary?
6. Use of the critical level concentration as the detection criterion[49].

How could this analysis and reporting have been improved?

The laboratory could have notified the customer that, although they could decay correct the parent nuclides to the date and time of sample collection, it is not possible to properly decay correct results for ^{140}La to the date of collection unless they assume that the pair had been in equilibrium at the time of collection. If the customer agreed with such an assumption, they should decay correct the result for the progeny to the time of collection using the half-life of the parent, clearly qualify the data, and note in the narrative the assumption that was made.

In any case, the activity, uncertainty, and critical level/MDC for ^{140}Ba should have been determined separately from ^{140}La using the most abundant gamma ray for ^{140}Ba at 537.3 keV (potentially with confirming lines at 162.7, 304.8, and/or 423.7 keV).

Finally, the data review process should also include a check of the reasonability of measured/reported results to verify that the measured data for the parent/progeny pairs conform to the ratios expected at equilibrium.

---

[49] The MDC is an *a priori* determination of activity concentration that can potentially be achieved. It does not take into account gamma ray interference corrections, or different backgrounds than a blank matrix sample. The critical level concentration should be used for 'detection' decisions (although in this case it did not matter).

Example 2: Results from the Irradiated Uranium PT

Laboratory		Activity Concentration, pCi/L			Activity Concentration, pCi/L		
		^{140}La	^{140}Ba	Measured Ratio/Theoretical (progeny/parent)	^{99m}Tc	^{99}Mo	Measured Ratio/Theoretical (progeny/parent)
1	Activity[1] at the start of the counting interval	1980	1879	1.05/ 1.13	---	---	---
	Corrected for decay back to time of collection	207,000	3457	59/1.00	1.0x10^{26}	5.03x10^{7}	2x10^{22}/0.96
2	Activity[1] at the start of the counting interval	---	---	---	---	---	---
	Corrected for decay back to time of collection	2.49x10^{6}	8.97x10^{3}	2.78x10^{2}/1.00	4.17x10^{19}	2.59x10^{3}	1.6x10^{16}/0.96

The results signified by "---" were reported only with decay corrected values so the activity concentrations at the start of the counting intervals were not available.

Figure 28. Parent Activity Inferred from Progeny; Progeny Half-Life Used for Its Decay Correction

Problems with results were found in the Irradiated Uranium PT results presented above (see Attachment 1 for details). These involved:

- making incorrect assumptions about equilibrium that resulted in the incorrect use of half-life for decay correction, and
- incorrectly performing an inferential determination of activity – one radionuclide was measured and the activity of the other radionuclide reported based on an assumed *secular* equilibrium concentration (which was incorrect as they are both transient equilibrium cases).

These results are shown in Figure 28.

The laboratory was instructed to decay correct results to the date of collection (and preservation). As noted in previous examples, ^{140}Ba/^{140}La and ^{99}Mo/^{99m}Tc form transient equilibrium pairs. If stable chemical conditions exist for approximately 15 days ^{140}Ba and ^{140}La will reach equilibrium, while approximately 2 days are needed for ^{99}Mo and ^{99m}Tc. Once equilibrium has been reached, the ratio of parent to progeny will approach the value characteristic of transient equilibrium for the pair. If the sample has reached equilibrium at the time of the count, it is no longer possible to make conclusions about what the activity would have been prior to the time of the count without making an assumption about when the sample reached equilibrium.

In this case, both pairs had sufficient time between the collection date and the count time to effectively reach transient equilibrium *(after ~11 days, assuming no ^{140}La at day zero, the ^{140}La:^{140}Ba ratio would be 1.13)*.

The principal gamma rays used for analysis of ^{140}Ba and ^{140}La were 487.0 keV and 1596.2 keV respectively (both lines are actually ^{140}La). The ^{99m}Tc line at 140.5 keV was used to measure both ^{99m}Tc and ^{99}Mo.

Although sufficient time had passed between sample collection and the count time for the samples to reach equilibrium, there would be no way to know that physical or chemical processes had not interfered with equilibrium *prior to* the preservation of the sample. Thus, the laboratory would have to assume that the pairs were in equilibrium at the point of collection if they wanted to decay correct the progeny activity *back to the time of the event* using the half-life of the parent. If on the other hand, the laboratory decay corrected the progeny activity using the half-life of the parent, they would have to assume that the sample had been in equilibrium at the point of collection. In some cases, this assumption is reasonable (e.g., ^{99}Mo and short-lived ^{99m}Tc) while in other cases, the situation may be less clear (e.g., ^{140}Ba and the longer-lived ^{140}La).

Prior to making such an assumption, it would always be advisable to contact the customer and let them know that decay correction would require an assumption. It would be imperative that, if the decay correction were performed, that the laboratory qualify the results and clearly document that they have made an assumption (e.g., in the case narrative).

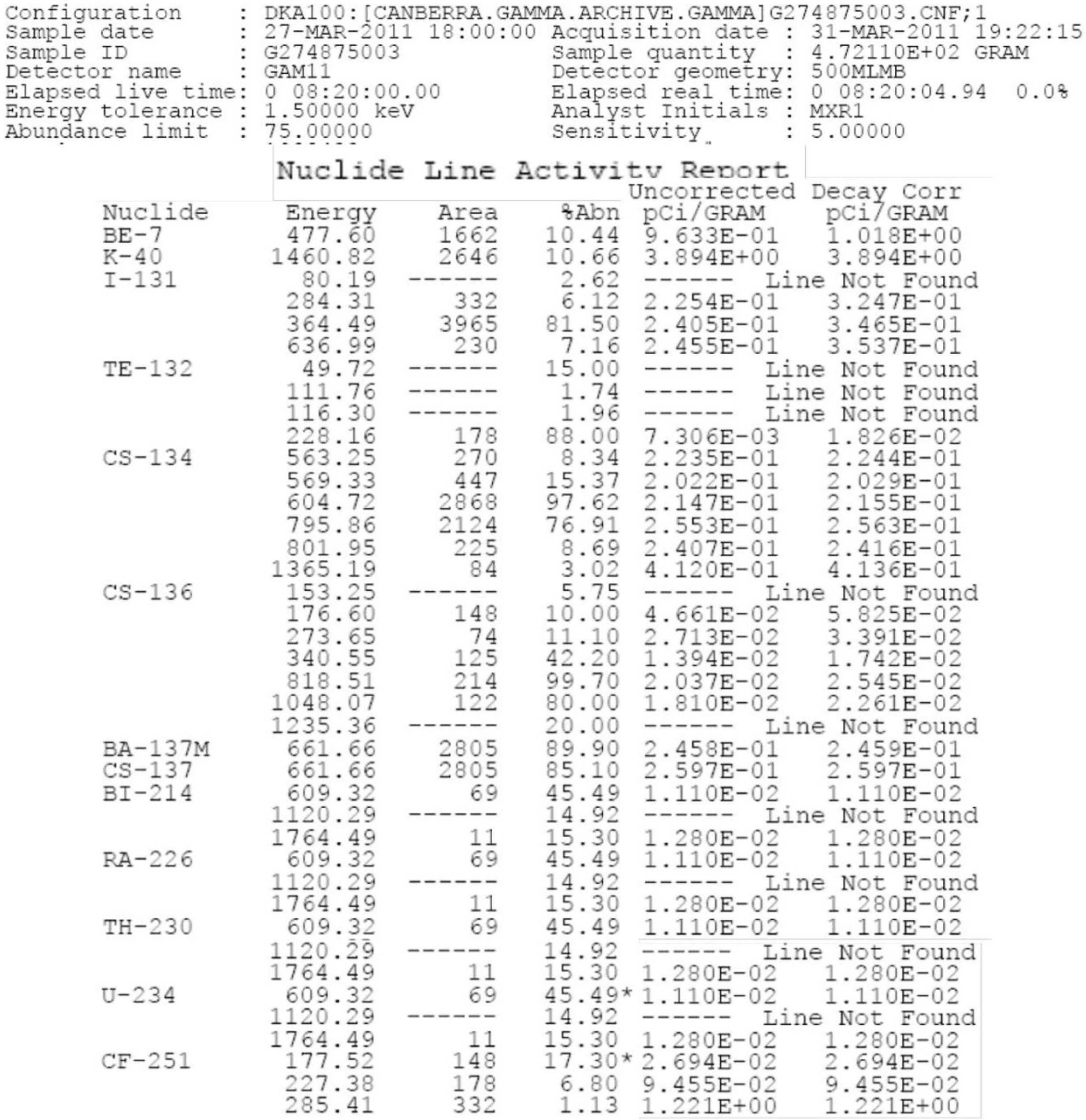
In this case, however, the decay corrected progeny activity was calculated using the half-life of the progeny even though the progeny activity was supported by a parent. The resulting decay corrected values for ^{140}La and ^{99m}Tc were extremely high and clearly unrealistic. Had the half-life of the parent been applied to the decay progeny, the ratios would have been within 10% of the theoretical ratio. While it would never be acceptable to decay correct the progeny results assuming they were unsupported, it might *not be* unreasonable to assume transient equilibrium was in place at the time of collection.

A second problem resulted since the laboratory used gamma rays emitted by the progeny to inferentially determine the activity of the parent. Even assuming that the pair was in equilibrium at the time of collection (and count), the laboratory incorrectly assumed that the pair were in *secular* equilibrium, and failed to adjust the activity of the parent to correctly reflect the expected ratio of activity of progeny to parent if equilibrium were established.

In both cases, however, using gamma rays directly attributable to the parent would have avoided the need to make an inferential determination based on the parent based on the activity of the progeny. Thus, the results for ^{140}Ba could have been determined using the most abundant gamma ray for ^{140}Ba with at 537.3 keV (potentially with confirming lines at 162.7, 304.8, 423.7 keV). Since ^{99}Mo emits a potentially interfering gamma ray at 537.8 keV (0.0033%), it would be important to enable interference corrections and to include the more abundant and reliable ^{99}Mo line at 739.5 keV in the library used for interference correction (even though the levels of interference of the low abundance ^{99}Mo gamma ray with the higher abundance gamma ray from ^{140}Ba may be minimal).

Finally, the data review process should also include a check of the reasonability of measured/reported results to verify that the measured data for the parent/progeny pairs conform to the ratios expected at equilibrium.

Example 3: Analysis of Miner's Lettuce Following the Fukushima Event-Incorrectly Identifying Radionuclide Gamma Rays



```
Configuration     : DKA100:[CANBERRA.GAMMA.ARCHIVE.GAMMA]G274875003.CNF;1
Sample date       : 27-MAR-2011 18:00:00 Acquisition date : 31-MAR-2011 19:22:15
Sample ID         : G274875003           Sample quantity  : 4.72110E+02 GRAM
Detector name     : GAM11                Detector geometry: 500MLMB
Elapsed live time: 0 08:20:00.00         Elapsed real time: 0 08:20:04.94  0.0%
Energy tolerance : 1.50000 keV           Analyst Initials : MXR1
Abundance limit   : 75.00000             Sensitivity      : 5.00000

                      Nuclide Line Activity Report
                                          Uncorrected Decay Corr
    Nuclide       Energy     Area     %Abn pCi/GRAM    pCi/GRAM
    BE-7          477.60     1662    10.44 9.633E-01   1.018E+00
    K-40         1460.82     2646    10.66 3.894E+00   3.894E+00
    I-131          80.19   ------     2.62 ------  Line Not Found
                  284.31      332     6.12 2.254E-01   3.247E-01
                  364.49     3965    81.50 2.405E-01   3.465E-01
                  636.99      230     7.16 2.455E-01   3.537E-01
    TE-132         49.72   ------    15.00 ------  Line Not Found
                  111.76   ------     1.74 ------  Line Not Found
                  116.30   ------     1.96 ------  Line Not Found
                  228.16      178    88.00 7.306E-03   1.826E-02
    CS-134        563.25      270     8.34 2.235E-01   2.244E-01
                  569.33      447    15.37 2.022E-01   2.029E-01
                  604.72     2868    97.62 2.147E-01   2.155E-01
                  795.86     2124    76.91 2.553E-01   2.563E-01
                  801.95      225     8.69 2.407E-01   2.416E-01
                 1365.19       84     3.02 4.120E-01   4.136E-01
    CS-136        153.25   ------     5.75 ------  Line Not Found
                  176.60      148    10.00 4.661E-02   5.825E-02
                  273.65       74    11.10 2.713E-02   3.391E-02
                  340.55      125    42.20 1.394E-02   1.742E-02
                  818.51      214    99.70 2.037E-02   2.545E-02
                 1048.07      122    80.00 1.810E-02   2.261E-02
                 1235.36   ------    20.00 ------  Line Not Found
    BA-137M       661.66     2805    89.90 2.458E-01   2.459E-01
    CS-137        661.66     2805    85.10 2.597E-01   2.597E-01
    BI-214        609.32       69    45.49 1.110E-02   1.110E-02
                 1120.29   ------    14.92 ------  Line Not Found
                 1764.49       11    15.30 1.280E-02   1.280E-02
    RA-226        609.32       69    45.49 1.110E-02   1.110E-02
                 1120.29   ------    14.92 ------  Line Not Found
                 1764.49       11    15.30 1.280E-02   1.280E-02
    TH-230        609.32       69    45.49 1.110E-02   1.110E-02
                 1120.29   ------    14.92 ------  Line Not Found
                 1764.49       11    15.30 1.280E-02   1.280E-02
    U-234         609.32       69    45.49*1.110E-02   1.110E-02
                 1120.29   ------    14.92 ------  Line Not Found
                 1764.49       11    15.30 1.280E-02   1.280E-02
    CF-251        177.52      148    17.30*2.694E-02   2.694E-02
                  227.38      178     6.80 9.455E-02   9.455E-02
                  285.41      332     1.13 1.221E+00   1.221E+00
```

Figure 29. Miners Lettuce Following Fukushima Event

The following concerns were noted on the final "Nuclide Line Activity Report" for the analysis of Miner's Lettuce following the Fukushima event (Figure 29):

1. The 177.52 keV gamma ray is used to identify ^{251}Cf in the sample. It was not possible for ^{251}Cf to be present in this sample. This is a library configuration error. Including nuclides in a library that are impossible or extremely unlikely to increase the risk of false detection of radionuclides.

2. The same peak area for a single gamma ray at 176.60 keV is used for both ^{136}Cs and ^{251}Cf. If two lines with the same energy are in a library and the interference correction is not enabled or is configured improperly, activity calculations will be incorrect. In this case, the activity is double counted by being attributed to two different nuclides.
3. The % abundance of the gamma ray at 661.66 keV is different for ^{137m}Ba and ^{137}Cs. The beta decay branch to the 661.66 keV excited state is 94.7%, however, in order to correctly calculate the activity of the ^{137m}Ba from the gamma emitted from that state, the reduced abundance (89.9% of the 94.7%) due to internal conversion must be taken into account; 85.10%.
4. The same gamma rays are used for ^{234}U, ^{226}Ra, and ^{230}Th and are not due to any of these radionuclides but to ^{214}Bi. Note that all these radionuclides have exactly the same activity, so it appears that the laboratory was assuming that the uranium decay chain was present in secular equilibrium. Since there is no basis for assuming secular equilibrium of the uranium chain in this matrix, these values are not defensible.
5. The sample transport time was 4 days. The non-volatile radionuclide, Te-132, is correctly identified. However in 4 days the progeny, ^{132}I should have been in transient equilibrium with the ^{132}Te. No gamma rays for ^{132}I were identified in the spectrum (one gamma ray from ^{132}I at 667 keV was detected but is in the unidentified lines list). In fact, during the 8-hour count interval the ratio of progeny to parent would have been close to 1.0; almost equilibrium. In this instance, the problem is lack of proper sample preservation. While it is impossible to know with certainty what happened prior to sampling, had the sample been preserved, any ^{132}I that was present would not have been able to volatilize as elemental iodine vapor prior to or during the count and iodine may have been determined as being present.
6. The abundance (or fraction) limit for this analysis was set at 75%. In other words, the summed abundance of lines identified in the sample divided by the sum of the abundance of all lines in the library must be 0.75 or greater before the software would consider the radionuclide identification to be valid. Using the library shown here and a limit of 75%, the software will conclude that ^{136}Cs is not present in the sample until three lines are identified including one that has only 42.2% abundance. In contrast, ^{131}I or ^{132}Te will require a single line with 82% or 88% abundance, respectively, to be considered valid.

Cs-134 Abnd.	Lines to ID
97.62	46%
76.91	83%
15.37	90%
8.69	95%
8.34	99%
3.02	100%

I-131 Abnd.	Lines to ID
81.5	84%
7.16	91%
6.12	97%
2.62	100%

Te-132 Abnd.	Lines to ID
88	82%
15	97%
1.96	98%
1.74	100%

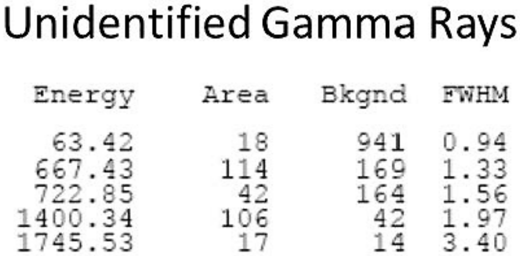
Cs-136 Abnd.	Lines to ID
99.7	37%
80	67%
42.2	83%
20	90%
11	94%
10	98%
5.75	1

Bi-214 Abnd.	Lines to ID
45.49	60%
15.3	80%
14.92	100%

This test proved to be unreliable for determining the presence of ^{136}Cs. It should probably have either been avoided (i.e., turned off), and one of the following functions enabled: a nuclide specific abundance limit, or key-lines to designate which lines are needed to constitute a valid identification.

7. An additional problem with the library usage is noted in the ‘Energy’ and ‘Area’ columns of Figure 29. Note that the following gamma ray and the same area have been used to calculate the activity of two different radionuclides: 177 keV with a peak area of 148 calculates an activity for both ^{136}Cs and ^{251}Cf. Cf-251 is not possible to be found in this sample and should not have been included in the analysis library. Also, note that the 177 peak has a significantly different activity and uncertainty for the ^{136}Cs activity as compared with its more reliable and abundant lines. Clearly, the 177 keV peak should not be used in the final analysis of ^{136}Cs.

Example 4: Unidentified Gamma Rays from Insufficient Library



```
Unidentified Gamma Rays

  Energy    Area   Bkgnd  FWHM

   63.42      18     941  0.94
  667.43     114     169  1.33
  722.85      42     164  1.56
 1400.34     106      42  1.97
 1745.53      17      14  3.40
```

Figure 30. Unidentified Gamma Rays from Miners Lettuce

1. The 667.43 line from ^{132}I was not identified due to an incorrectly constructed library.
2. The library listed the key line for ^{132}I as the 772.6 keV gamma ray which is a less abundant gamma-ray energy. Although ^{132}I was present, it was considered not detected since the 772.6 keV gamma ray was not detected. The laboratory staff should have identified this problem when reviewing unidentified peaks, but their review process failed to properly attribute the activity at 667.43 keV to ^{132}I.
3. The 1400 keV photon is a coincidence sum peak from ^{134}Cs. This should be included in the library as a “sum peak” or at least should have been noted as such in the laboratory’s raw data.
4. The 1745 keV peak may be eliminated as a real gamma ray due to a wide FWHM (3.4 keV). Given the low number of counts, this can be attributed to poor fitting of data for the statistically weak peak.
5. In general, all unidentified lines should be resolved by the analyst or reviewer prior to sending out a final report. Any gamma rays that cannot be attributed to a radionuclide, an artifact of the other gamma rays in the spectrum, or determined to be of poor quality or exceptionally high uncertainty should be entered into the laboratory’s condition reporting system to be researched and resolved.

Example 5: Incorrect Radionuclide Equilibrium Used to Analyze Rainwater Samples from Fukushima

Sample Date	Analysis Date	I-132 µCi/mL	Te-132 µCi/mL	Ratio ^{132}I/^{132}Te
3/19/2011 9:00	3/22/2011	(8.52 ± 3.25)x10^{-9}	(1.18 ± 0.40)x10^{-8}	7.22E-01
3/21/2011 11:00	3/24/2011	(1.92±0.49)x10^{-8}	(2.40±0.66)x10^{-8}	8.00E-01
3/21/2011 10:00	3/24/2011	(2.27±0.39)x10^{-8}	(2.83±0.59)x10^{-8}	8.02E-01
3/21/2011 8:00	3/23/2011	(2.04±0.48)x10^{-8}	(2.49±0.55)x10^{-8}	8.19E-01
3/24/2011 14:36	3/28/2011	(1.63±0.46)x10^{-8}	(2.49±0.73)x10^{-8}	6.55E-01
3/24/2011 14:30	3/28/2011	1.99±0.45)x10^{-8}	(2.56±0.66)x10^{-8}	7.77E-01
3/24/2011 8:00	3/28/2011	(8.35±6.09)x10^{-9}	(1.25±0.54)x10^{-8}	6.68E-01
3/25/2011 9:30	3/30/2011	ND	(1.96±0.72)x10^{-8}	0.00E+00
3/25/2011 9:00	3/30/2011	(2.32±0.70)x10^{-8}	(2.50±0.74)x10^{-8}	9.28E-01
3/25/2011 8:00	3/30/2011	(6.76±5.61)x10^{-9}	(1.04±0.52)x10^{-8}	6.50E-01
3/28/2011 9:13	3/31/2011	(7.19±3.64)x10^{-9}	(6.98±6.35)x10^{-9}	1.03E+00
3/28/2011 9:00	3/31/2011	ND	(8.08±4.30)x10^{-9}	0.00E+00

Figure 31. Rainwater Samples Following Fukushima Event

This table shows an example of radiochemical equilibrium disturbed by chemical effects in rainwater samples collected following the Fukushima incident and analyzed by gamma spectrometry within a few days of being taken. It may have been advantageous to count these samples somewhat longer to reduce the uncertainties which range from about 35 to 90%.

The theoretical ratio for ^{132}I/^{132}Te is 1.03 when equilibrium has been established. The samples were not preserved and sent in plastic containers. The time between sampling and analysis was more than sufficient for transient equilibrium to have been established in the sample. At the time it was assumed that there would be insignificant losses for such a short transport time and subsequent analysis. The low values for the ratios are likely due to loss of iodine either due to volatilization or deposition on the container walls as I_2.

Following the Fukushima event, several air samples were analyzed by gamma spectrometry. The transient equilibrium pair ^{140}Ba/^{140}La was determined to be undetected. However, the gamma spectrometry report[50] in each case had the *same exact values* for calculated activity concentration, uncertainty, and LLD (to three significant figures) for both of these radionuclides. This is an extremely improbable situation. As can be seen in Table 4, the activity ratio should be 1.15 for ^{140}La/^{140}Ba when equilibrium has been established. The reason this occurred was that the library contained interfering lines and the software had *not* been configured to perform interference correction so that these two activity calculations used the same peak area(s) data to calculate the activity. In addition, the secular equilibrium case was assumed (in the library) instead of the transient equilibrium case.

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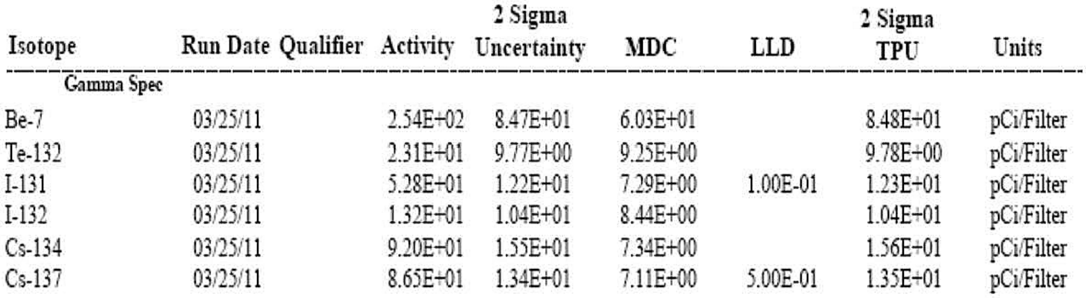
[50] See Attachment II Figure 27 for the excerpt from this report

Example 6: Incorrect Preservation of Samples and Its Effect on Analysis



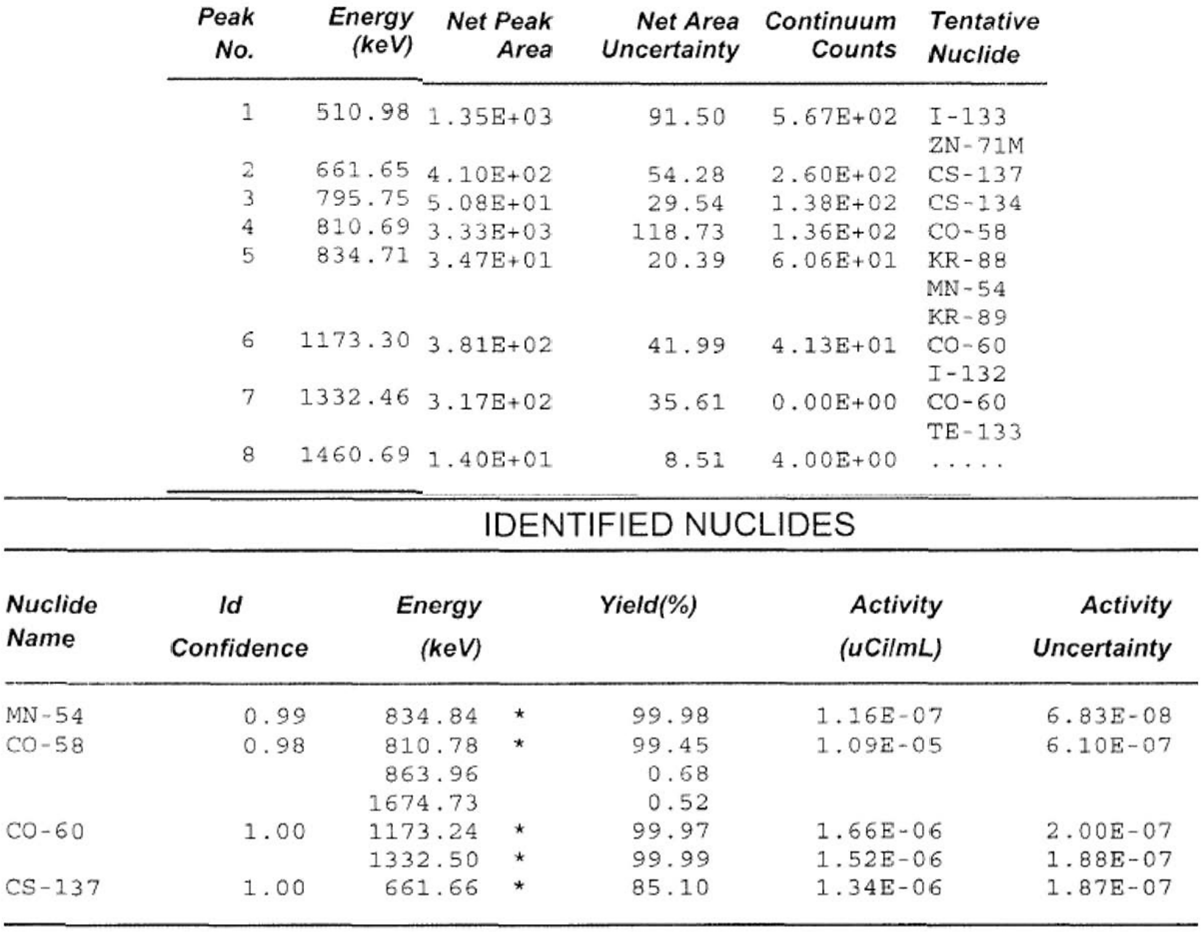
Isotope	Run Date	Qualifier	Activity	2 Sigma Uncertainty	MDC	LLD	2 Sigma TPU	Units
Gamma Spec								
Be-7	03/25/11		2.54E+02	8.47E+01	6.03E+01		8.48E+01	pCi/Filter
Te-132	03/25/11		2.31E+01	9.77E+00	9.25E+00		9.78E+00	pCi/Filter
I-131	03/25/11		5.28E+01	1.22E+01	7.29E+00	1.00E-01	1.23E+01	pCi/Filter
I-132	03/25/11		1.32E+01	1.04E+01	8.44E+00		1.04E+01	pCi/Filter
Cs-134	03/25/11		9.20E+01	1.55E+01	7.34E+00		1.56E+01	pCi/Filter
Cs-137	03/25/11		8.65E+01	1.34E+01	7.11E+00	5.00E-01	1.35E+01	pCi/Filter

Figure 32. Dry Deposition Samples Following Fukushima Event

A similar situation of ^{132}I being 'lost' due to volatilization (as in Figure 32) occurred with samples taken in the same area by "sticky" pad for dry deposition. The sticky pad sample sheet was removed from the stack and folded into itself to prevent the deposited material from sloughing off. It was then shipped in a Ziploc™ bag to the contract laboratory.

The time period between sampling and gamma spectrometry analysis was approximately 3 days. The ratio of ^{132}I/^{132}Te calculated from the above data is 0.57. With a half-life of 2.3 hours, there was ample time for the ^{132}I to reach equilibrium prior to the analysis. The activity ratio at equilibrium is 1.03. Clearly, the preservation technique for this type of sample needs to include a means of preventing iodine loss due to volatilization.

Example 7: Incorrect Abundance



```
 Peak    Energy  Net Peak        Net Area   Continuum  Tentative
  No.     (keV)      Area     Uncertainty      Counts  Nuclide

   1     510.98  1.35E+03           91.50    5.67E+02  I-133
                                                       ZN-71M
   2     661.65  4.10E+02           54.28    2.60E+02  CS-137
   3     795.75  5.08E+01           29.54    1.38E+02  CS-134
   4     810.69  3.33E+03          118.73    1.36E+02  CO-58
   5     834.71  3.47E+01           20.39    6.06E+01  KR-88
                                                       MN-54
                                                       KR-89
   6    1173.30  3.81E+02           41.99    4.13E+01  CO-60
                                                       I-132
   7    1332.46  3.17E+02           35.61    0.00E+00  CO-60
                                                       TE-133
   8    1460.69  1.40E+01            8.51    4.00E+00  .....

                          IDENTIFIED NUCLIDES

Nuclide        Id          Energy        Yield(%)       Activity      Activity
Name       Confidence       (keV)                       (uCi/mL)    Uncertainty

MN-54         0.99         834.84   *      99.98        1.16E-07       6.83E-08
CO-58         0.98         810.78   *      99.45        1.09E-05       6.10E-07
                           863.96           0.68
                          1674.73           0.52
CO-60         1.00        1173.24   *      99.97        1.66E-06       2.00E-07
                          1332.50   *      99.99        1.52E-06       1.88E-07
CS-137        1.00         661.66   *      85.10        1.34E-06       1.87E-07
```

Figure 33. Waste Liquid Release Sample

The peak search algorithm used for analysis of the sample identified in Figure 33, found a peak at 795 keV, and tentatively identified it as ^{134}Cs (note that the peak has a relatively high uncertainty). However, the abundance limit function for this analysis was selected at 90%.

The method of calculation for this check is as follows:

$$\% \, Abundance \; Found = \frac{\sum_i^n A_i}{\sum_i^n A_L}$$

Where:

A_i is the abundance of the gamma rays identified by the software in the sample

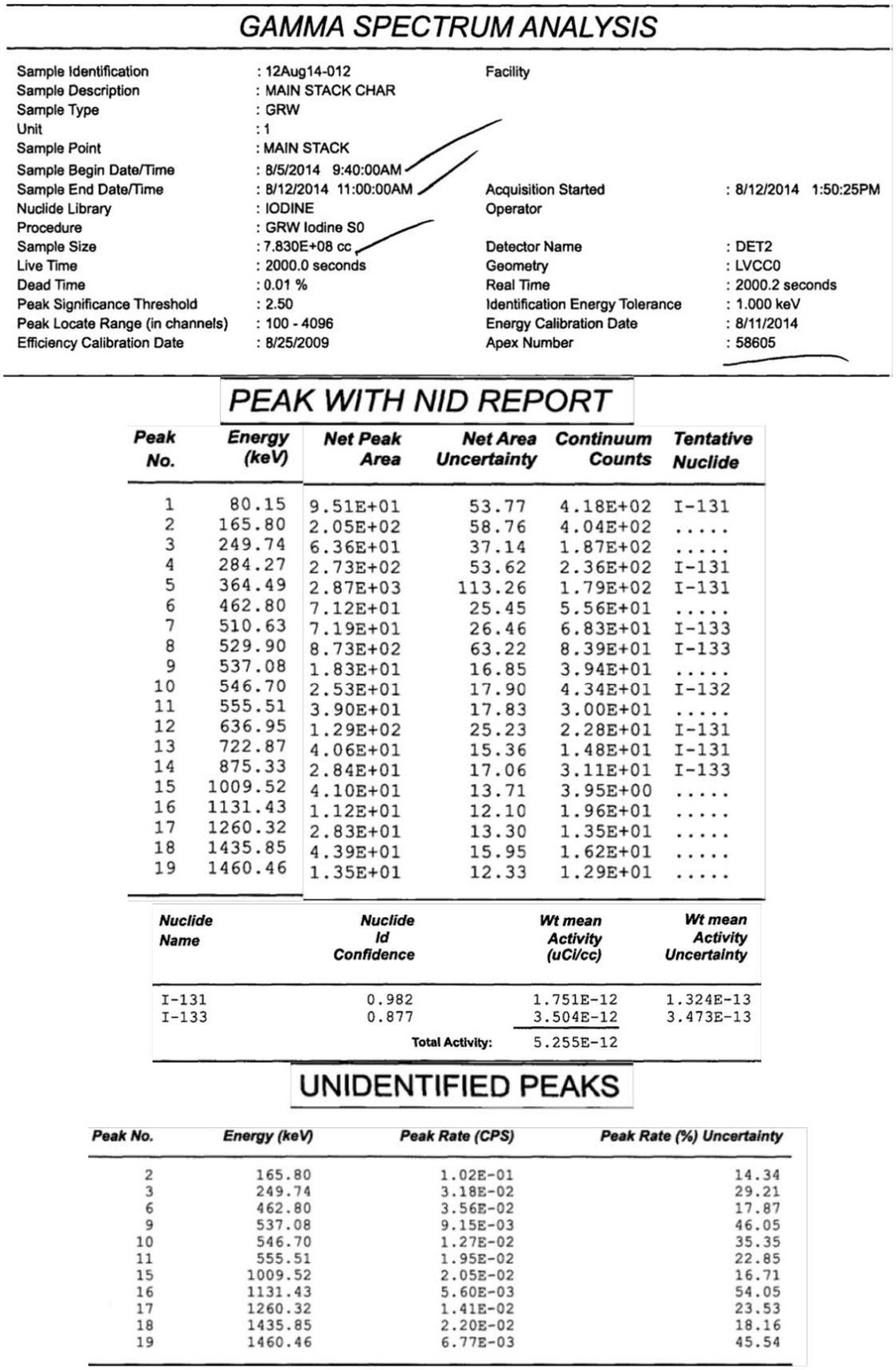
A_L is the sum of all the abundances for gamma rays listed in the library.

The 795 keV peak is 85% abundant. The 604 keV peak has a 97% abundance but was not detected. So even if the 795 and the 604 peaks were the only ones in the library, the peak would not have been identified as ^{134}Cs since, 85/(85+97) = 46.7%. Since no other peaks were found the "Identified Nuclides" list does not include ^{134}Cs. Inspection of the spectrum indicated that the reason for that gamma ray not being detected is that it sits on top of the Compton Edge for the 810 keV gamma ray from ^{58}Co. This raised the background sufficiently so that the peak was not distinguishable. Had this peak been detected and correctly identified the abundance limit would have been exceeded {(85% +97%)> 90%} and the software would have been determined that the radionuclide was identified. The peak at 796 keV is interference free. The gamma ray at 604 keV also suffers from interferences due to ^{125}Sb (a fission product) at 601 keV and ^{124}Sb (a direct fission product and also an activation product) at 603 keV. For ^{134}Cs it may be a better option to either choose the 796 keV gamma ray as the keV (even though it is less abundant).

This emphasizes the importance of correlating the gamma spectrometry report for unidentified peaks with what is visible on the spectrum in relation to potential interferences. It bears repeating that the abundance or fraction test generally should not be used for libraries containing more than a single radionuclide,

Also, note that a 1460 keV peak was detected, but not identified. This is because ^{40}K was not present in the library used for this analysis. While the ^{40}K was an expected radionuclide in such a sample (as a naturally-occurring radionuclide from water in contact with a concrete sump) the library did not reflect this fact. Review of unidentified peaks should have but failed to identify this problem. Including ^{40}K in a suspect library would help alleviate such a situation.

Example 8: Software Preset Functions and Radionuclide Misidentification and Unidentification



```
                         GAMMA SPECTRUM ANALYSIS

Sample Identification               : 12Aug14-012            Facility
Sample Description                  : MAIN STACK CHAR
Sample Type                         : GRW
Unit                                : 1
Sample Point                        : MAIN STACK
Sample Begin Date/Time              : 8/5/2014   9:40:00AM
Sample End Date/Time                : 8/12/2014  11:00:00AM  Acquisition Started             : 8/12/2014   1:50:25PM
Nuclide Library                     : IODINE                 Operator
Procedure                           : GRW Iodine S0
Sample Size                         : 7.830E+08 cc           Detector Name                   : DET2
Live Time                           : 2000.0 seconds         Geometry                        : LVCC0
Dead Time                           : 0.01 %                 Real Time                       : 2000.2 seconds
Peak Significance Threshold         : 2.50                   Identification Energy Tolerance : 1.000 keV
Peak Locate Range (in channels)     : 100 - 4096             Energy Calibration Date         : 8/11/2014
Efficiency Calibration Date         : 8/25/2009              Apex Number                     : 58605

                          PEAK WITH NID REPORT

 Peak    Energy   Net Peak       Net Area    Continuum   Tentative
  No.     (keV)       Area    Uncertainty       Counts   Nuclide

   1      80.15   9.51E+01          53.77     4.18E+02   I-131
   2     165.80   2.05E+02          58.76     4.04E+02   .....
   3     249.74   6.36E+01          37.14     1.87E+02   .....
   4     284.27   2.73E+02          53.62     2.36E+02   I-131
   5     364.49   2.87E+03         113.26     1.79E+02   I-131
   6     462.80   7.12E+01          25.45     5.56E+01   .....
   7     510.63   7.19E+01          26.46     6.83E+01   I-133
   8     529.90   8.73E+02          63.22     8.39E+01   I-133
   9     537.08   1.83E+01          16.85     3.94E+01   .....
  10     546.70   2.53E+01          17.90     4.34E+01   I-132
  11     555.51   3.90E+01          17.83     3.00E+01   .....
  12     636.95   1.29E+02          25.23     2.28E+01   I-131
  13     722.87   4.06E+01          15.36     1.48E+01   I-131
  14     875.33   2.84E+01          17.06     3.11E+01   I-133
  15    1009.52   4.10E+01          13.71     3.95E+00   .....
  16    1131.43   1.12E+01          12.10     1.96E+01   .....
  17    1260.32   2.83E+01          13.30     1.35E+01   .....
  18    1435.85   4.39E+01          15.95     1.62E+01   .....
  19    1460.46   1.35E+01          12.33     1.29E+01   .....

 Nuclide              Nuclide            Wt mean        Wt mean
 Name                      Id           Activity       Activity
                   Confidence           (uCi/cc)    Uncertainty

 I-131                  0.982          1.751E-12      1.324E-13
 I-133                  0.877          3.504E-12      3.473E-13
                      Total Activity:  5.255E-12

                          UNIDENTIFIED PEAKS

Peak No.     Energy (keV)     Peak Rate (CPS)     Peak Rate (%) Uncertainty

   2            165.80           1.02E-01                 14.34
   3            249.74           3.18E-02                 29.21
   6            462.80           3.56E-02                 17.87
   9            537.08           9.15E-03                 46.05
  10            546.70           1.27E-02                 35.35
  11            555.51           1.95E-02                 22.85
  15           1009.52           2.05E-02                 16.71
  16           1131.43           5.60E-03                 54.05
  17           1260.32           1.41E-02                 23.53
  18           1435.85           2.20E-02                 18.16
  19           1460.46           6.77E-03                 45.54
```

Figure 34. Radioiodine Analysis of a Charcoal Cartridge

The excerpts above are from the analysis of a charcoal cartridge that was used to sample a nuclear power plant vent for one week. Several different preset functions play into radionuclide misidentification in this sample analysis. The results have been decay corrected to the mid-point of the sampling interval (3.5 days prior to the analysis). Four of the unidentified peaks belong to ^{135}I. Four of the unidentified peaks belong to ^{138}Cs. The report header is missing information regarding the half-life ratio function which was selected as the default value of 12. The library selected was the "Iodine" library. Why were ^{135}I and ^{138}Cs not identified? The ratio of decay from sample time to radionuclide half-life was in excess of 12; (3.5 days x24 hours per day/6.57 hours) = 12.8. Thus the software eliminated ^{135}I as a possible radionuclide based on the logic that its half-life is too short to be present after 12 half-lives. But this function does not take into account that the sample was counted only *two hours after it was removed* from the active sample line. I-135 was being continuously released to the plant vent during the sampling interval. Thus the half-life ratio preset function should not have been used. This error in the use of the preset function caused a released radionuclide not to be reported properly. Decay correcting to the midpoint of the sampling interval is recommended for this process but as in this case may not always be appropriate.

The correct time to be used as a reference for decay correction should be reconsidered.

Four of the unidentified gamma rays, 1009, 1435, 547 and 462 keV, belong to ^{138}Cs. While the particulate filter that precedes the charcoal cartridge normally captures this as particulate, ^{138}Xe, which is also present in the plant vent effluent, is the precursor to ^{138}Cs, and the xenon gas has an affinity for the charcoal cartridge. The library chosen for analysis of this spectrum was "Iodine" which did not contain either ^{138}Xe or ^{138}Cs as one of its entries. Furthermore, even if they had been in the library, their short half-lives (14 and 32 minutes, respectively) would have prevented the software from identifying them for the same reason the ^{135}I was not identified. Review of the unidentified peaks report in the spectrum should have caught the fact that these peaks had been disqualified, and led to resolution of the issue (using an appropriate library and increasing or disabling the half-life test).

Example 9: Effect of Differing Chemistry of Parent and Progeny

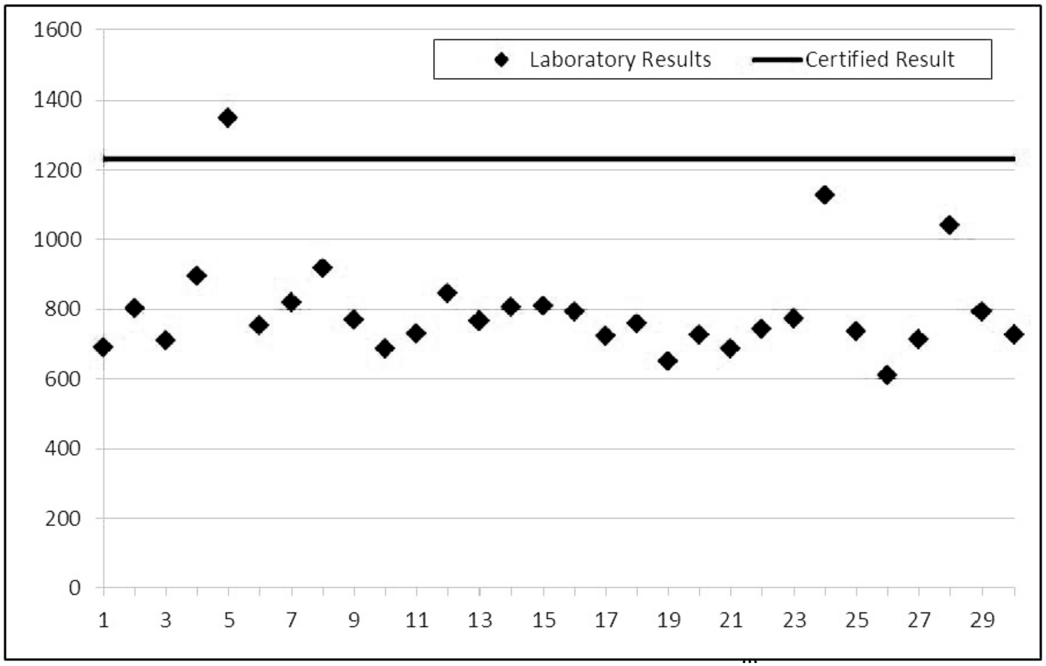


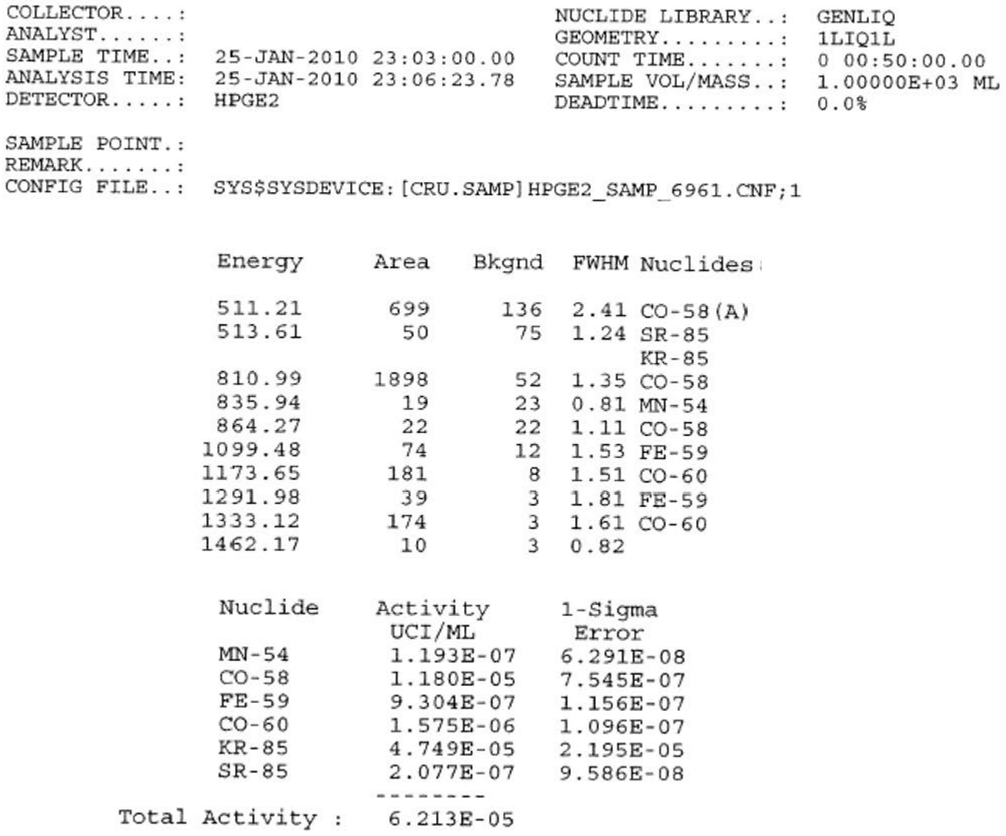
Figure 35. Proficiency Test Results for ^{95}Zr

A fission product PT sample was prepared by dissolving irradiated uranium. Aliquants of the final solution were sent to various laboratories for analysis (see instructions sent to laboratories in Attachment 1). The method of sample dissolution and subsequent dilution for distribution did not take into account the solubility characteristics of one of the radionuclides, ^{95}Zr (the solution should have been preserved with fluoride to complex the zirconium maintaining it in solution). The laboratory that prepared the PT samples performed multiple analyses of replicates of the undiluted solution so that the activity concentrations for 16 radionuclides could be used as a reference for comparison with the participating laboratories. Their analyses were performed very shortly after the undiluted solution was dissolved. The laboratories received the diluted samples about a two weeks later. The results are shown in Figure 35 for ^{95}Zr with all 30 participating laboratories results included. The average value from the participating laboratories was biased ~34% low compared to the reference laboratory value.

The disparity of the reference value versus a single laboratory result was investigated by one of the participating laboratories and by the contract laboratory. The participating laboratory had performed a partial transfer of the sample to their own gamma spectrometry geometry without any additional chemical means. They recounted the original shipping container after it had been emptied and found residual ^{95}Zr. It was discovered that a substantial portion of the ^{95}Zr had either settled or plated out in the shipping container. The contract laboratory had examined the same possibility and obtained similar results. It was recognized that preservation of the sample would need to include fluoride ion to ensure that zirconium did not precipitate out on the container surfaces.

Analysis results like these emphasize the importance of preservation of samples even over short periods of time.

Example 10: Incomplete Preset Library to Detect Gamma Rays



```
COLLECTOR....:                                   NUCLIDE LIBRARY..:  GENLIQ
ANALYST......:                                   GEOMETRY.........:  1LIQ1L
SAMPLE TIME..:  25-JAN-2010 23:03:00.00          COUNT TIME.......:  0 00:50:00.00
ANALYSIS TIME:  25-JAN-2010 23:06:23.78          SAMPLE VOL/MASS..:  1.00000E+03 ML
DETECTOR.....:  HPGE2                            DEADTIME.........:  0.0%

SAMPLE POINT.:
REMARK.......:
CONFIG FILE..:  SYS$SYSDEVICE:[CRU.SAMP]HPGE2_SAMP_6961.CNF;1

                Energy      Area    Bkgnd   FWHM Nuclides

                511.21       699      136   2.41 CO-58(A)
                513.61        50       75   1.24 SR-85
                                                 KR-85
                810.99      1898       52   1.35 CO-58
                835.94        19       23   0.81 MN-54
                864.27        22       22   1.11 CO-58
               1099.48        74       12   1.53 FE-59
               1173.65       181        8   1.51 CO-60
               1291.98        39        3   1.81 FE-59
               1333.12       174        3   1.61 CO-60
               1462.17        10        3   0.82

                Nuclide     Activity        1-Sigma
                            UCI/ML           Error
                MN-54        1.193E-07     6.291E-08
                CO-58        1.180E-05     7.545E-07
                FE-59        9.304E-07     1.156E-07
                CO-60        1.575E-06     1.096E-07
                KR-85        4.749E-05     2.195E-05
                SR-85        2.077E-07     9.586E-08
                             --------
         Total Activity :    6.213E-05
```

Figure 36. One Gamma Ray Used for two Radionuclides

This sample was a waste liquid release from a nuclear power plant. The library used was their general liquid library which included all the main library radionuclides. The annihilation peak was seemingly resolved from the 513 keV gamma ray by the software and tentatively identified as either ^{85}Kr or ^{85}Sr. However, the FWHM of the annihilation peak had an effect on the background in the 513 keV peak, likely causing its area to be underestimated. The ^{85}Kr activity was calculated but was likely underestimated due to the potential overlap from the annihilation peak.

To start, this library should not have been used since ^{85}Sr cannot possibly be present in the waste liquid of a pressurized water reactor (it is neither an activation product of reactor materials nor is it a fission product). Similarly, the identification and quantitation as ^{85}Sr should have been rejected in the review process as incorrect and the radionuclide to which it truly belonged identified. Since more than one radionuclide used the same gamma ray to calculate the activity, it is unclear whether the software apportioned the peak between the two radionuclides (i.e., via deconvolution of the peak or interference correction) or whether is used the same area counts for both.

The 1462 keV peak is from ^{40}K. This radionuclide and other naturally occurring radionuclides should be included in the waste liquid library as many of the waste streams can come into contact with concrete and leach these radionuclides from the concrete. If ^{40}K is really not of concern, including it in the suspect library would at least help facilitate identification of the unidentified line. Some software packages have the ability to qualitatively identify a gamma ray without including it for quantitation.

The only gamma ray for ^{58}Co that should have been used in the calculation was the 810 keV gamma ray. While the “(A)” notation indicates that the 511 peak is annihilation radiation, the library contained a user added abundance factor, and thus the 511 peak was used in the activity concentration calculation. The areas for improvement for this analysis are:

- Revision of library to:
  - Better address gamma rays with gamma rays that have energies that are close to each other
  - Remove any improbable radionuclides from the individual sample stream library
  - Use only true gamma ray lines for ^{58}Co
- The review process also needs to be improved to include basic facts about radionuclides that can be present in the system and those which cannot.
- The energy calibration, and possibly the shape (resolution) calibration could be improved. This certainly led to the 1462 peak being off by 1.2 keV and may have led to the overlap at 511 and 514 keV.

Example 11: Sample-Source Geometry Mismatch

Figure 37. Sample Containers of Similar but Different Size and Composition

Figure 37 shows a number of different sample containers that a laboratory used to count samples using one sample to detector geometry. Although the containers are close in size and shape, they do not have exactly the same dimensions. Additionally, they are made of different plastics with different wall thicknesses. The standard (not shown) used to calibrate the detector was prepared in a container that matched the clear plastic ones seen in the figure. Also disconcerting was the sample containers were filled to different levels.

This situation represents a sample-calibration source mismatch. Samples analyzed under this condition will have an unknown, but definite bias.

Example 12: Incorrect Placement of Samples in Detectors

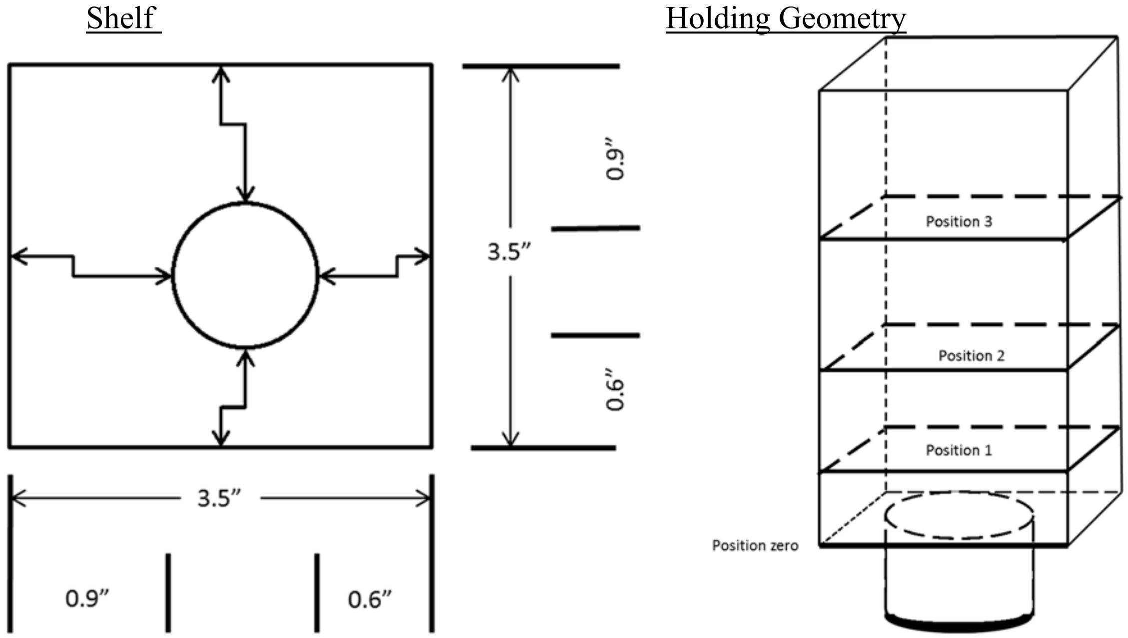


Figure 38. Sample Container Geometry Holder

The sketch of a sample container holder shown in Figure 38 is based on an assessment of a laboratory’s count room practices. The dimensions of the holder show that the circular groove for fitting a charcoal cartridge or air particulate filter was not exactly centered on the square shelf used to hold it. None of the edges were marked to show which edge should be placed in the same position when counting a sample. Additionally, there were nine of these shelves for 3 different detectors, with three different sample holding geometries also shown in Figure 37. Position zero was fixed in the holding geometry; the shelves were unmarked so any shelf could be used in any holding geometry on any detector. The holding geometries were not assigned to a specific detector and showed signs of physical wear at each surface contact point. It is also important to keep in mind that in HPGe detectors, the germanium crystal is quite frequently not perfectly centered under the detector protective “can”.

The result of these minor inconsistencies is a potential for sample-to-standard geometry mismatch unless the same holding geometry is assigned to a specific detector and each shelf is coded so that it has one position on a specific holding geometry. There was no such coding at this laboratory and results from some PT samples are seen in Figure 39 A, B, and C.

Example 13: Incorrect Placement of Samples in Detectors and Sample Bias

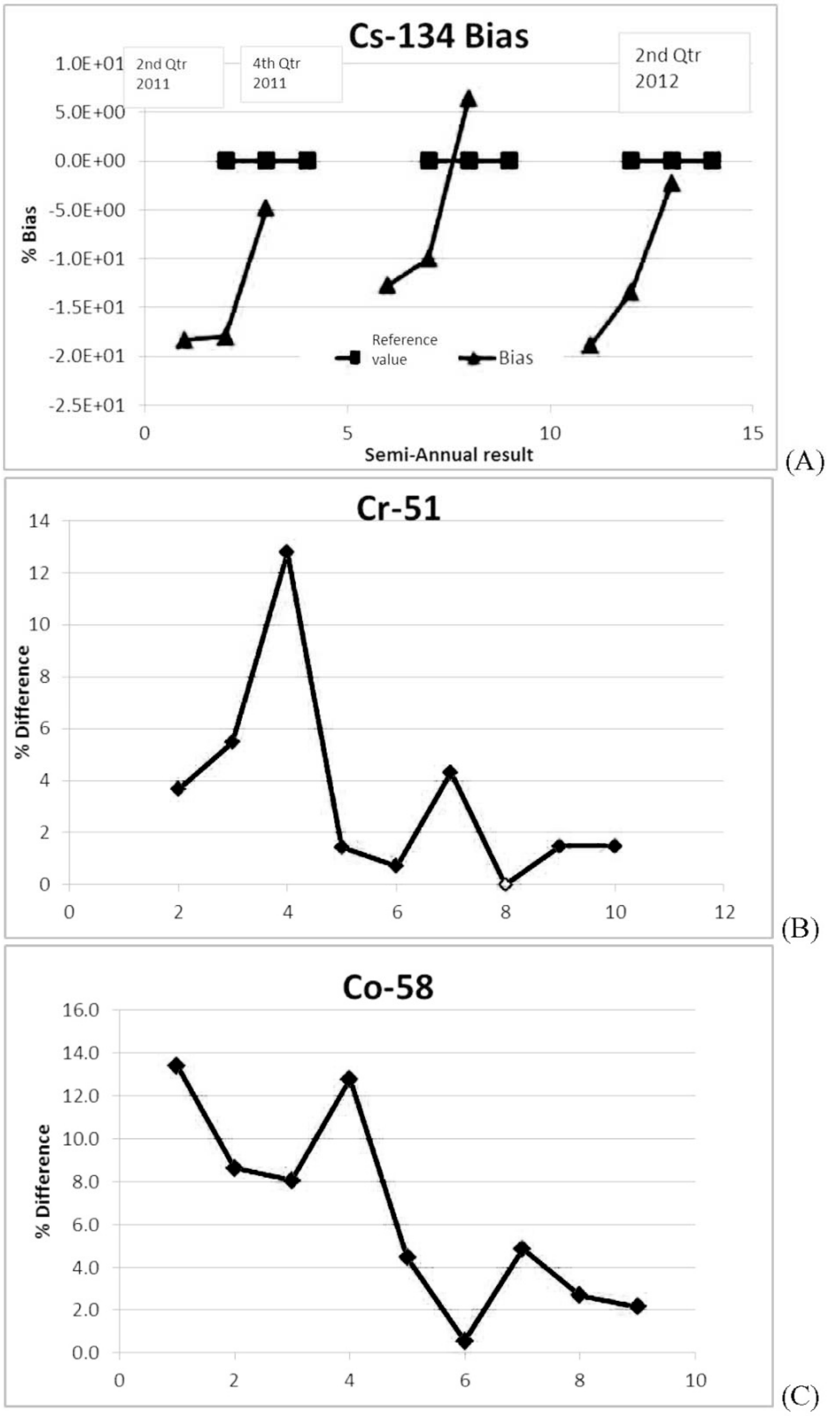


Figure 39. Incorrect Geometry Leads to Bias

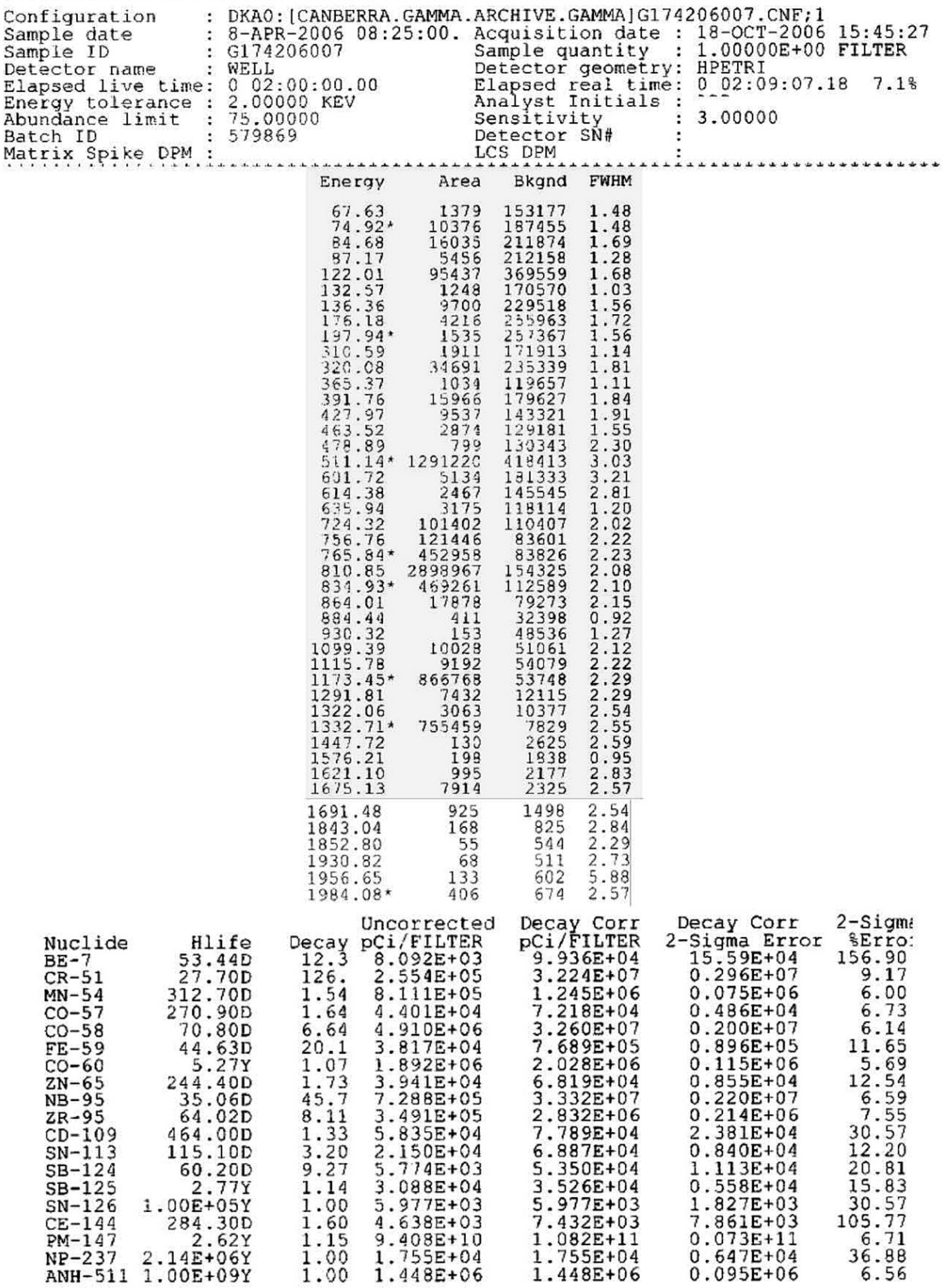
The graphs above show the % Bias or % Difference for aqueous PT samples containing several radionuclides (only three are shown here as an example). The activity concentrations for all three were in the range of 1×10^{7} to 2×10^{8} pCi/L (1×10^{-2} to 2×10^{-1} µCi/mL).

The principal gamma rays for ^{134}Cs suffer from the coincidence sum effect. This causes the results of activity for this radionuclide to be biased negative. The closer the sample is to the detector the larger will be the negative bias. This effect cannot be accounted for in any simple manner. Figure 39 (A) shows results for PT samples for an air particulate filter geometry.

For each quarter-year period shown in Figure 39A, the distance from the sample to detector increases from left to right. It can be seen that the bias for the ^{134}Cs measurements decreases with distance that the sample is counted from the detector. The bias in these results was exacerbated by the sample holder used to 'center' these filters on the detector (see Figure 38). A mispositioning of the sample holder likely caused the +5% bias of the 4th quarter 2011 sample on the farthest shelf from the detector.

Figures 39 (B) and (C) show the results for ^{51}Cr and ^{58}Co in the same PT sample. The percent difference in these analyses is very wide for samples that had a relatively high activity (i.e., low uncertainty due to counting). Both radionuclides have gamma rays of good abundance and, in these samples; there are no interfering gamma rays from other radionuclides. These results were not trended, and the laboratory staff had accepted all these analyses as satisfactory.

Example 14: Incorrect Use of Half-Lives and Inappropriate Detector



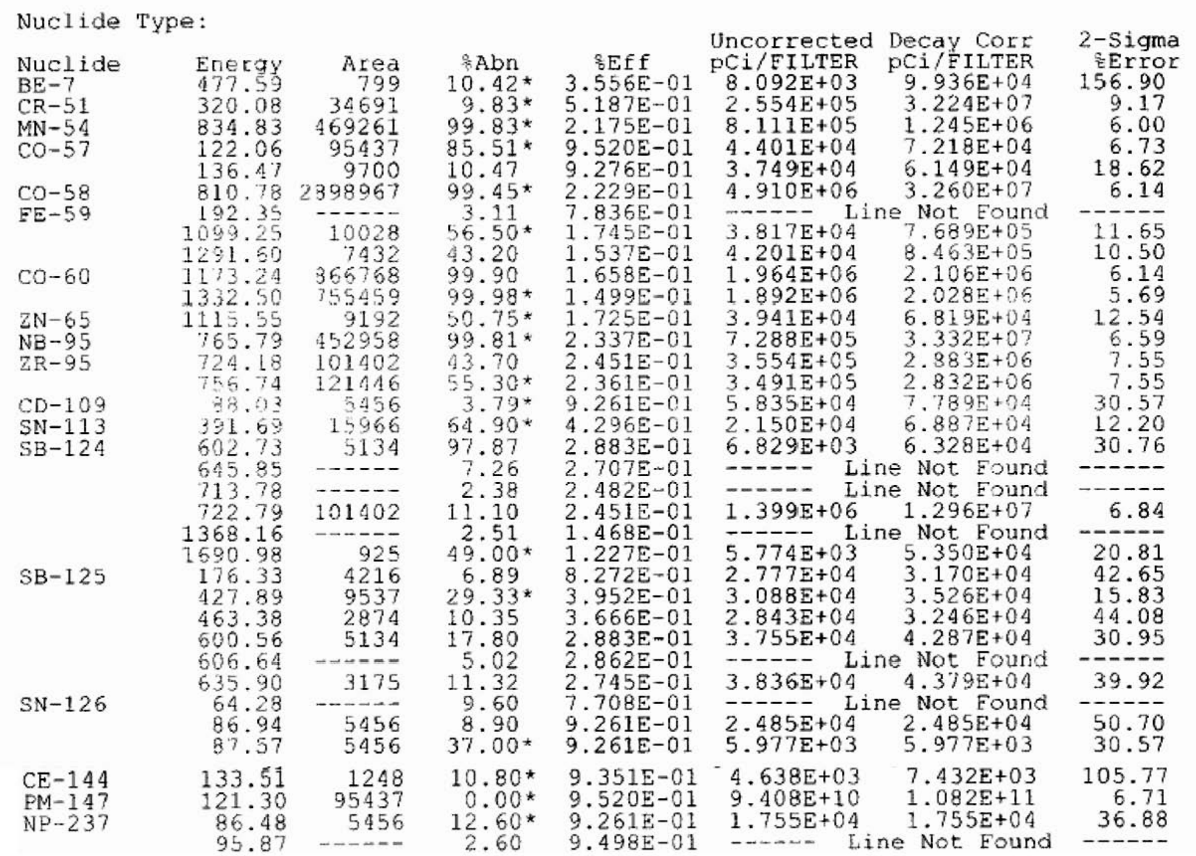
```
***************************************************************************************
Configuration       : DKA0:[CANBERRA.GAMMA.ARCHIVE.GAMMA]G174206007.CNF;1
Sample date         : 8-APR-2006 08:25:00. Acquisition date : 18-OCT-2006 15:45:27
Sample ID           : G174206007           Sample quantity  : 1.00000E+00 FILTER
Detector name       : WELL                 Detector geometry: HPETRI
Elapsed live time: 0 02:00:00.00           Elapsed real time: 0 02:09:07.18  7.1%
Energy tolerance : 2.00000 KEV             Analyst Initials : ---
Abundance limit  : 75.00000                Sensitivity      : 3.00000
Batch ID         : 579869                  Detector SN#     :
Matrix Spike DPM :                         LCS DPM          :
***************************************************************************************
                     Energy     Area    Bkgnd  FWHM

                      67.63     1379   153177  1.48
                      74.92*   10376   187455  1.48
                      84.68    16035   211874  1.69
                      87.17     5456   212158  1.28
                     122.01    95437   369559  1.68
                     132.57     1248   170570  1.03
                     136.36     9700   229518  1.56
                     176.18     4216   255963  1.72
                     197.94*    1535   257367  1.56
                     310.59     1911   171913  1.14
                     320.08    34691   235339  1.81
                     365.37     1034   119657  1.11
                     391.76    15966   179627  1.84
                     427.97     9537   143321  1.91
                     463.52     2874   129181  1.55
                     478.89      799   130343  2.30
                     511.14* 1291220   418413  3.03
                     601.72     5134   181333  3.21
                     614.38     2467   145545  2.81
                     635.94     3175   118114  1.20
                     724.32   101402   110407  2.02
                     756.76   121446    83601  2.22
                     765.84*  452958    83826  2.23
                     810.85  2898967   154325  2.08
                     834.93*  469261   112589  2.10
                     864.01    17878    79273  2.15
                     884.44      411    32398  0.92
                     930.32      153    48536  1.27
                    1099.39    10028    51061  2.12
                    1115.78     9192    54079  2.22
                    1173.45*  866768    53748  2.29
                    1291.81     7432    12115  2.29
                    1322.06     3063    10377  2.54
                    1332.71*  755459     7829  2.55
                    1447.72      130     2625  2.59
                    1576.21      198     1838  0.95
                    1621.10      995     2177  2.83
                    1675.13     7914     2325  2.57
                    1691.48      925     1498  2.54
                    1843.04      168      825  2.84
                    1852.80       55      544  2.29
                    1930.82       68      511  2.73
                    1956.65      133      602  5.88
                    1984.08*     406      674  2.57

                              Uncorrected   Decay Corr    Decay Corr     2-Sigm
Nuclide        Hlife   Decay  pCi/FILTER    pCi/FILTER  2-Sigma Error    %Erro
BE-7          53.44D   12.3   8.092E+03     9.936E+04    15.59E+04     156.90
CR-51         27.70D   126.   2.554E+05     3.224E+07    0.296E+07       9.17
MN-54        312.70D   1.54   8.111E+05     1.245E+06    0.075E+06       6.00
CO-57        270.90D   1.64   4.401E+04     7.218E+04    0.486E+04       6.73
CO-58         70.80D   6.64   4.910E+06     3.260E+07    0.200E+07       6.14
FE-59         44.63D   20.1   3.817E+04     7.689E+05    0.896E+05      11.65
CO-60          5.27Y   1.07   1.892E+06     2.028E+06    0.115E+06       5.69
ZN-65        244.40D   1.73   3.941E+04     6.819E+04    0.855E+04      12.54
NB-95         35.06D   45.7   7.288E+05     3.332E+07    0.220E+07       6.59
ZR-95         64.02D   8.11   3.491E+05     2.832E+06    0.214E+06       7.55
CD-109       464.00D   1.33   5.835E+04     7.789E+04    2.381E+04      30.57
SN-113       115.10D   3.20   2.150E+04     6.887E+04    0.840E+04      12.20
SB-124        60.20D   9.27   5.774E+03     5.350E+04    1.113E+04      20.81
SB-125         2.77Y   1.14   3.088E+04     3.526E+04    0.558E+04      15.83
SN-126     1.00E+05Y   1.00   5.977E+03     5.977E+03    1.827E+03      30.57
CE-144       284.30D   1.60   4.638E+03     7.432E+03    7.861E+03     105.77
PM-147         2.62Y   1.15   9.408E+10     1.082E+11    0.073E+11       6.71
NP-237     2.14E+06Y   1.00   1.755E+04     1.755E+04    0.647E+04      36.88
ANH-511    1.00E+09Y   1.00   1.448E+06     1.448E+06    0.095E+06       6.56
```

Figure 40. Progeny Decay Correction with Incorrect Half-Life

This gamma-ray analysis is of a filter sample from a nuclear power plant. The filter was used to remove radioactivity from the reactor coolant system (RCS). This means it removed fission as well as activation products from the RCS. The filter was used to process liquid through an entire 18-month fuel cycle. The filter was allowed to decay in the storage container for at least two months prior to the sample of the filter being removed on the 8th of April 2006. The sample resided at the power plant until the beginning of October 2006 and sent offsite to be analyzed.



```
Nuclide Type:
                                                         Uncorrected  Decay Corr    2-Sigma
Nuclide      Energy      Area     %Abn       %Eff        pCi/FILTER   pCi/FILTER    %Error
BE-7         477.59       799    10.42*    3.556E-01     8.092E+03    9.936E+04    156.90
CR-51        320.08     34691     9.83*    5.187E-01     2.554E+05    3.224E+07      9.17
MN-54        834.83    469261    99.83*    2.175E-01     8.111E+05    1.245E+06      6.00
CO-57        122.06     95437    85.51*    9.520E-01     4.401E+04    7.218E+04      6.73
             136.47      9700    10.47     9.276E-01     3.749E+04    6.149E+04     18.62
CO-58        810.78   2398967    99.45*    2.229E-01     4.910E+06    3.260E+07      6.14
FE-59        192.35    ------     3.11     7.836E-01     ------ Line Not Found     ------
            1099.25     10028    56.50*    1.745E-01     3.817E+04    7.689E+05     11.65
            1291.60      7432    43.20     1.537E-01     4.201E+04    8.463E+05     10.50
CO-60       1173.24    866768    99.90     1.658E-01     1.964E+06    2.106E+06      6.14
            1332.50    755459    99.98*    1.499E-01     1.892E+06    2.028E+06      5.69
ZN-65       1115.55      9192    50.75*    1.725E-01     3.941E+04    6.819E+04     12.54
NB-95        765.79    452958    99.81*    2.337E-01     7.288E+05    3.332E+07      6.59
ZR-95        724.18    101402    43.70     2.451E-01     3.554E+05    2.883E+06      7.55
             756.74    121446    55.30*    2.361E-01     3.491E+05    2.832E+06      7.55
CD-109        88.03      5456     3.79*    9.261E-01     5.835E+04    7.789E+04     30.57
SN-113       391.69     15966    64.90*    4.296E-01     2.150E+04    6.887E+04     12.20
SB-124       602.73      5134    97.87     2.883E-01     6.829E+03    6.328E+04     30.76
             645.85    ------     7.26     2.707E-01     ------ Line Not Found     ------
             713.78    ------     2.38     2.482E-01     ------ Line Not Found     ------
             722.79    101402    11.10     2.451E-01     1.399E+06    1.296E+07      6.84
            1368.16    ------     2.51     1.468E-01     ------ Line Not Found     ------
            1690.98       925    49.00*    1.227E-01     5.774E+03    5.350E+04     20.81
SB-125       176.33      4216     6.89     8.272E-01     2.777E+04    3.170E+04     42.65
             427.89      9537    29.33*    3.952E-01     3.088E+04    3.526E+04     15.83
             463.38      2874    10.35     3.666E-01     2.843E+04    3.246E+04     44.08
             600.56      5134    17.80     2.883E-01     3.755E+04    4.287E+04     30.95
             606.64    ------     5.02     2.862E-01     ------ Line Not Found     ------
             635.90      3175    11.32     2.745E-01     3.836E+04    4.379E+04     39.92
SN-126        64.28    ------     9.60     7.708E-01     ------ Line Not Found     ------
              86.94      5456     8.90     9.261E-01     2.485E+04    2.485E+04     50.70
              87.57      5456    37.00*    9.261E-01     5.977E+03    5.977E+03     30.57

CE-144       133.51      1248    10.80*    9.351E-01     4.638E+03    7.432E+03    105.77
PM-147       121.30     95437     0.00*    9.520E-01     9.408E+10    1.082E+11      6.71
NP-237        86.48      5456    12.60*    9.261E-01     1.755E+04    1.755E+04     36.88
              95.87    ------     2.60     9.498E-01     ------ Line Not Found     ------
```

Figure 41. Energy Lines from Gamma-ray Analysis of a Filter

As can be seen in the header information, the sample was placed into a Petri dish and counted using a well-type detector on October 18, 2006. The dead time was about 7%. The FWHM of the peaks located by the software is wide, as expected, compared to a non-well-type detector (and it is likely the high dead time also contributed to this factor). The use of a well-type detector for the analysis of high activity samples such as this one also leads to larger and greater varieties of random sum peaks (such as the ones at 1621 and 1322 keV, both from ^{58}Co). In this instance, a planar p-type HPGE would have been better suited for the analysis as there may be low abundance gamma rays from other radionuclides that are not seen due to the wide FWHM of the high activity gamma rays.

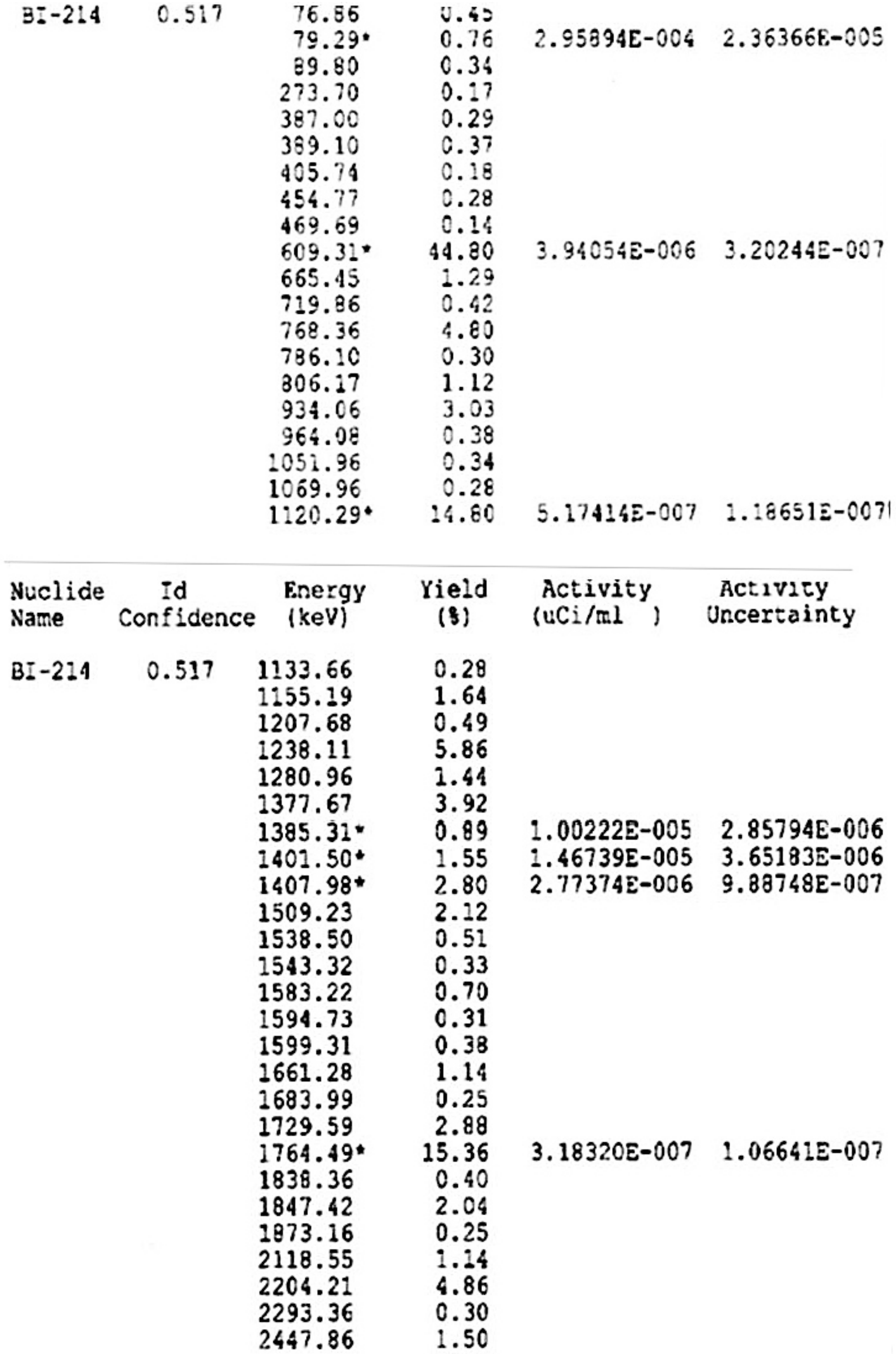
The half-lives used for the analysis are listed in the second column in Figure 40. Note that the ^{95}Nb activity concentration was calculated using a 34-day half-life. The ratio of the ^{95}Nb/^{95}Zr activity should be about 2.2, as they are well into their transient equilibrium when the sample was taken. The activity ratio from the report excerpt above is 11.73. If the activity of ^{95}Nb activity is decay corrected using the 64.02-day half-life of ^{95}Zr, the corrected activity is 5.76×10^6 pCi/filter, and the ^{95}Nb/^{95}Zr ratio is 2.035, in much better agreement with the theoretical value of 2.2.

In addition to the half-life issue, the same gamma-ray lines were used to calculate the activity of several different radionuclides as seen in Figure 41. Specifically: ^{109}Cd, ^{237}Np, ^{126}Sn were all calculated using *the same area* under the 87 keV peak. Co-57 and ^{147}Pm were both calculated from the same area under the 121 keV peak. Also, note that the peaks under ^{126}Sn at 86.94 and 87.57 are displayed with the same peak areas.

These issues can be avoided if:

- The library is constructed to resolve interferences, and interference correction features are properly configured and enabled for that analysis protocol
- Alternate key lines are chosen for those radionuclides identified in the sample
- Radionuclides that cannot be found in the sample are eliminated from the sample-specific protocol library

Example 15: Incorrect Identification of Gamma Rays from Insufficient Libraries and Incorrect Identification of Peaks



```
BI-214    0.517      76.86     0.45
                     79.29*    0.76    2.95894E-004  2.36366E-005
                     89.80     0.34
                    273.70     0.17
                    387.00     0.29
                    389.10     0.37
                    405.74     0.18
                    454.77     0.28
                    469.69     0.14
                    609.31*   44.80    3.94054E-006  3.20244E-007
                    665.45     1.29
                    719.86     0.42
                    768.36     4.80
                    786.10     0.30
                    806.17     1.12
                    934.06     3.03
                    964.08     0.38
                   1051.96     0.34
                   1069.96     0.28
                   1120.29*   14.80    5.17414E-007  1.18651E-007
-----------------------------------------------------------------
Nuclide    Id        Energy    Yield    Activity     Activity
Name    Confidence   (keV)     (%)     (uCi/ml  )   Uncertainty

BI-214    0.517    1133.66     0.28
                   1155.19     1.64
                   1207.68     0.49
                   1238.11     5.86
                   1280.96     1.44
                   1377.67     3.92
                   1385.31*    0.89    1.00222E-005  2.85794E-006
                   1401.50*    1.55    1.46739E-005  3.65183E-006
                   1407.98*    2.80    2.77374E-006  9.88748E-007
                   1509.23     2.12
                   1538.50     0.51
                   1543.32     0.33
                   1583.22     0.70
                   1594.73     0.31
                   1599.31     0.38
                   1661.28     1.14
                   1683.99     0.25
                   1729.59     2.88
                   1764.49*   15.36    3.18320E-007  1.06641E-007
                   1838.36     0.40
                   1847.42     2.04
                   1873.16     0.25
                   2118.55     1.14
                   2204.21     4.86
                   2293.36     0.30
                   2447.86     1.50
```

Figure 42. Proficiency Test Sample Spiked with Fission Products

This is an excerpt taken from a gamma-ray report for analysis of a proficiency test sample that was spiked with some fission and activation products. The PT sample had the following radionuclides at the reference activity concentrations listed here:

	^{95}Zr	^{95}Nb	^{103}Ru	^{106}Ru	^{110m}Ag	^{131}I	^{134}Cs	^{137}Cs	^{139}Ce	^{141}Ce	^{152}Eu
Accepted Value, pCi/L	38132	73800	29560	401	424	131400	3948	211	2014	68020	252

The laboratory staff had never dealt with anything but environmental samples with only NORM radionuclides. The sample had been counted for a relatively short period of time compared to their normal environmental samples, and this sample did not have any measurable NORM. The final activity (4.53×10^{-7} µCi/mL) was determined by using the weighted mean of all the peaks the software identified as belonging to ^{214}Bi. The review of the sample did not identify that the range of values varied from 2.95×10^{-4} to 3.18×10^{-7} µCi/mL. As one of the first steps in the review process, seeing if the data make sense may have started the unraveling of this data to yield true gamma-ray identities.

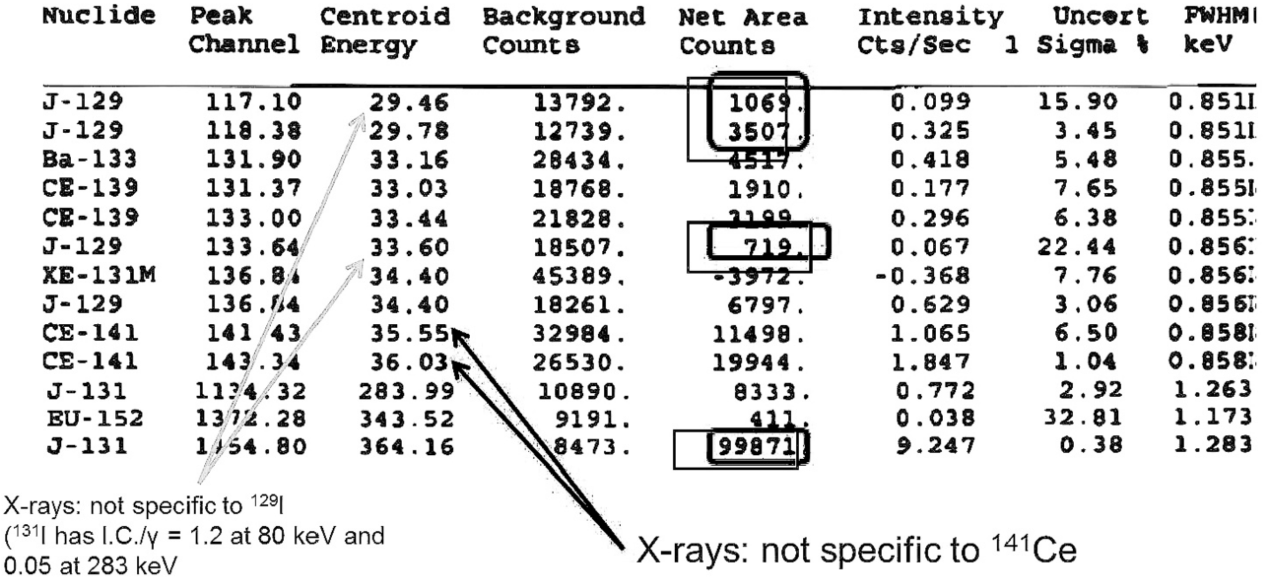
The only gamma rays that are associated with the background ^{214}Bi activity are the peaks at 1764 and 1120 keV. Both yield activities that are reasonably close in activity concentration.

The following peaks should be associated with other gamma-ray emitters:

- The 79.29 keV gamma ray is a 2.6% abundance peak from ^{131}I (only the most abundant ^{131}I gamma ray at 364 was in the library)
- The 609.3 keV peak is from ^{103}Ru (was not in the library)
- The 1120 keV peak is a random sum peak from ^{131}I and ^{95}Nb (364 +756 keV) and contributed to the peak area causing that activity to be larger than the activity calculated for the 1764 keV peak.
- The 1385.3 keV peak is from ^{110m}Ag (this radionuclide was not in the library and all the other more prominent peaks from this radionuclide were sent to the unidentified lines report)
- The 1401 keV peak is a coincidence sum peak from ^{134}Cs
- The 1407.9 keV peak is from ^{152}Eu (not in library, more prominent gammas went to the unidentified lines report)

The results of this report could have been improved if the library had been adjusted to recognize the fission products and activation products that would likely have been in the sample. A more thorough review should have been performed of the individual line activities (which would have identified discrepancies in the activities) and also the potential for the random and coincidence sum effects creating interferences in identification and quantification.

Example 16: Incorrectly Identified Gamma Rays Based on Energies



Nuclide	Peak Channel	Centroid Energy	Background Counts	Net Area Counts	Intensity Cts/Sec	1	Uncert Sigma %	FWHM keV
J-129	117.10	29.46	13792.	1069.	0.099		15.90	0.851
J-129	118.38	29.78	12739.	3507.	0.325		3.45	0.851
Ba-133	131.90	33.16	28434.	4517.	0.418		5.48	0.855.
CE-139	131.37	33.03	18768.	1910.	0.177		7.65	0.855
CE-139	133.00	33.44	21828.	2199.	0.296		6.38	0.855
J-129	133.64	33.60	18507.	719.	0.067		22.44	0.856
XE-131M	136.84	34.40	45389.	-3972.	-0.368		7.76	0.856
J-129	136.84	34.40	18261.	6797.	0.629		3.06	0.856
CE-141	141.43	35.55	32984.	11498.	1.065		6.50	0.858
CE-141	143.34	36.03	26530.	19944.	1.847		1.04	0.858
J-131	1134.32	283.99	10890.	8333.	0.772		2.92	1.263
EU-152	1372.28	343.52	9191.	411.	0.038		32.81	1.173
J-131	1454.80	364.16	8473.	99871.	9.247		0.38	1.283

X-rays: not specific to ^{129}I
(^{131}I has I.C./γ = 1.2 at 80 keV and
0.05 at 283 keV

X-rays: not specific to ^{141}Ce

Figure 43. Analysis of a PT Fission Product Sample Using X-ray Region

In this specific example, the X-rays of iodine were used to determine ^{129}I a very long-lived isotope of radioiodine, and the X-rays of cerium were used for ^{141}Ce analysis instead of using the 145 keV gamma ray (which was not identified). Since X-rays of I or Ce are representative of *any* isotope of that element, they are not useful for identification or quantification of any specific isotope.

Note the net area counts highlighted in yellow for the various iodine peaks that were identified. The counts for the 29.46 and 33.6 keV peaks if *only* attributable to one radioiodine would have been ~1880 and 1030 counts, respectively. The gamma rays emitted by ^{131}I at 80 and 283 keV have internal conversion ratios of 0.05 and 1.2, respectively; thus both yield significant X-rays which cannot be associated with ^{129}I.

Both these analyses were significantly biased by the shorter-lived, higher activity radioisotopes of the other isotopes, Xe and Pr, the progeny of multiple iodine and cerium fission products present in the sample.

An additional issue with this analysis was that the detector was calibrated between 59 and 1837 keV. Thus quantitative assessment of activity concentration outside of that energy range is not valid.

Example 17: How Progeny Activity Can Be Used To Calculate Parent Activity

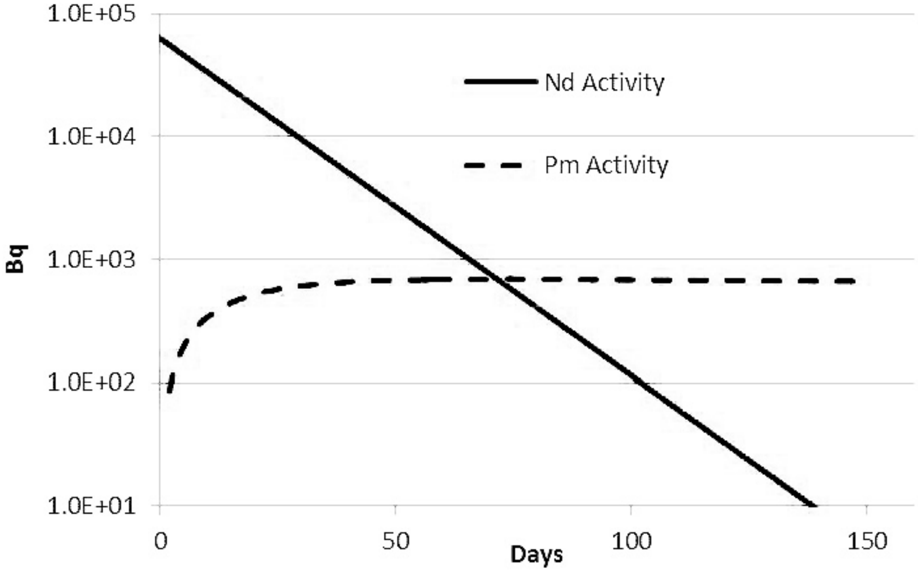


Figure 44. Pm-147 Detected 20 Days Following an Event

A sample taken 20 days after an IND event[51] was recounted and found to contain 6.86x10^6 Bq/g of ^{147}Pm. During the initial analysis, the ^{147}Nd peak at 91.1 keV was interfered with by a large set of ^{234}Th X-rays at 92.2-92.8 keV. A better value for the ^{147}Nd was requested by the incident command to correctly assess the dose during the early phase of the incident.

This example is not from real data but presented here to show how the progeny of a "no equilibrium" case can also be used to calculate the activity of a parent that has decayed away.

In this instance, the sample is counted 80 days following the initial event. The assumptions are:

- The 1-liter soil sample was collected in a Marinelli beaker
- It was collected approximately 2 hours following the incident and was analyzed immediately (thus there was negligible ingrowth of the ^{147}Pm at that time)
- The sample was subsequently preserved in a temperature controlled room for 80 days and recounted

The equation that relates the activity of progeny to parent at any time, t, is (Equation 6):

$$A_2^1 = A_2^0 e^{-\lambda_2 t} + A_1^0 \left(\frac{\lambda_2}{\lambda_2 - \lambda_1}\right)\left(e^{-\lambda_1 t} - e^{-\lambda_2 t}\right)$$

In this instance, however, the activity of the progeny is known at 80 days and it is necessary to calculate the initial activity of parent.

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[51] An IND that contained both enriched and natural uranium was detonated. The natural uranium had fully ingrown ^{234}Th.

Rearranging the above equation we can calculate the activity of ^{147}Nd at time zero.

$$A_1^0 = \frac{\left(A_2^1 - A_2^0 \times e^{-\lambda_2 t}\right) \times (\lambda_2 - \lambda_1)}{\lambda_2 \times (e^{-\lambda_1 t} - e^{-\lambda_2 t})}$$

The term $A_2^0 \times e^{-\lambda_2 t}$ is assumed to be zero at 2 hours post event since the direct (independent) fission yield, A_2^0, of this radionuclide is very small (< $2.5\text{x}10^{-6}$%) compared to the production from the decay of its short-lived progenitors. Substituting in the equation we find:

$$A_1^0 = \frac{\left(6.86\text{x}10^6 \; - 0 \times e^{-7.23x10^{-4} \times 80}\right) \times (7.23x10^{-4} - 6.31x10^{-2})}{7.23x10^{-4} \times \left(e^{-6.31x10^{-2} \times 80} - e^{-7.23x10^{-4} \times 80}\right)} = 6.31 \times 10^8 \, Bq$$