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Radiochemical Analysis Methodology for Uranium Depletion Measurements

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NOTICE

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ABSTRACT

This report provides sufficient material for a test sponsor with little or no radiochemistry background to understand and follow physics irradiation test program execution. Most irradiation test programs employ similar techniques and the general details provided here can be applied to the analysis of other irradiated sample types. Aspects of program management directly affecting analysis quality are also provided.

This report is not an in-depth treatise on the vast field of radiochemical analysis techniques and related topics such as quality control. Instrumental technology is a very fast growing field and dramatic improvements are made each year, thus the instrumentation described in this report is no longer cutting edge technology. Much of the background material is still applicable and useful for the analysis of older experiments and also for subcontractors who still retain the older instrumentation.

ACKNOWLEDGMENTS

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ACRONYMS AND TERMS

List of Acronyms and Terms Used in This Report

ADC	Analog to digital converter
ALARA	As low as reasonably achievable
DOE	Department of Energy
EDTA	Ethylene diamine tetra-acetic acid
EPA	Environmental Protection Agency
FP	Fission Product
ICPMS	Inductively coupled plasma mass spectrometer
ICPAES	Inductively coupled plasma atomic emission spectrometer
IDMS	Isotope dilution mass spectrometry
LLD	Lower limit of detection
MCA	Multichannel analyzer
MDA	Minimum detectable activity
MDL	Minimum detection limit
NIM	Nuclear Instrumentation Module
NIST	National Institute of Standards and Technology
RCRA	Resource Conservation and Recovery Act
TIMS	Thermal ionization mass spectrometer
TRU	Transuranic nuclide
WIPP	Waste Isolation Pilot Plant

SYMBOLS AND FORMULAE

CHEMICAL & MATHEMATICAL SYMBOLS AND FORMULAE USED IN REPORT

2σ	2 sigma error: ~95% probability the correct result lies within the experimental error bars
Am	Americium
amu	Atomic mass unit
B	Boron
Bq	Becquerel = SI unit replacing curies = one disintegration/second = 2.703×10^{-11} Ci
Ce	Cerium
Ci	Curie = 3.700×10^{10} disintegration/seconds
Cm	Curium
cpm	Counts per minute
cps	Counts per second
Cr	Chromium
Cs	Cesium
Eu	Europium
Fe	Iron
g	Grams
Ge	Germanium
HF	Hydrofluoric acid
HIO_3	Iodic acid
HO_2CCO_2H	Oxalic acid
La	Lanthanum
mg	Milligram (0.001 gram)
μg	Microgram (0.000001 gram)
M	Molar = concentration of a solute: number of moles of solute per liter of solution
$Na_2S_2O_7$	Sodium pyrosulfate
Nd	Neodymium
Ni	Nickel
Np	Neptunium
Pm	Promethium
ppm	Parts per million (typically micrograms of analyte per gram of material)
Pr	Praseodymium
Pu	Plutonium
Re	Rhenium
Rh	Rhodium
Ru	Ruthenium
Sm	Samarium
U	Uranium
W	Tungsten

RADIOCHEMICAL ANALYSIS METHODOLOGY FOR URANIUM DEPLETION MEASUREMENTS

I. Introduction

This document provides a general overview of the radiochemical analytical techniques used for the destructive testing of irradiated test specimens. The background material for radiochemical analytical techniques[a] is covered by the following sections:

- sampling issues,
- sample characteristics,
- background on overall process,
- dissolution techniques,
- reference materials and blanks,
- radiochemical separation and purification processes,
- instrumental analyses,
- quality control for radiochemical analytical laboratories,
- trouble shooting experimental problems, and
- lessons learned and best practices.

The measured species of interest is referred to as the analyte. Unless otherwise specified, all analytes are measured and reported quantitatively[b] in terms of grams or atoms of analyte per test specimen. Also note that the majority of the analytes are the individual isotopes of chemical elements (isotopic analysis) rather than a composite of all isotopes of a given element (elemental analysis).

This document focuses only on the current techniques and methods[c] for common analytes measured for irradiated test specimens where uranium is not the major test specimen component. The discussion is not inclusive of all possible analytes nor all possible experimental methodologies. Additional background information is provided in the following appendices:

A. Experimental Design and Follow

B. Common Calculations

C. Experimental Error Analysis

D. Radiochemical Analytical Techniques: Pitfalls & Enlightenment

These appendices provide either more in-depth background for the topics of the various sections, or provide useful auxiliary information for program management of a physics irradiation test program. Currently, all radiochemical analytical measurements of physics irradiation test programs are performed by subcontractors.

This document is based on the experience of several decades of sponsoring radiochemical measurements of highly enriched uranium depletion samples for the Naval Nuclear Propulsion Program.

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a. Physical or chemical principles utilized separately or in combination with other techniques to determine the composition of the analyte. For example: thermal ionization mass spectrometry is a technique.
b. Also known as “absolute” measurements.
c. An assemblage of measurement techniques and the order in which they are used.

II. Sampling Issues

The sampling process is not a component of the radiochemical analytical technique. However, proper sampling, processing and tracking is vital to the success of the downstream radiochemical analytical techniques, and thus the ultimate success of the experimental test program. If the subcontractor receives test specimens that are compromised in any way, the resource intensive measurements will be unusable.

A. Sampling Process

The sampling method for the removal of test specimens from irradiated materials is dependent upon the physical form of the irradiated material, the desired physical form of the resulting test specimen, and the experimental requirements. Sampling methods and their associated components (types of samples, sampling plan, sampling equipment, sampling containers, sampling procedures, sample recording, sample chain of custody requirements, etc.) will not be discussed here.

There are common components for any sampling method for the provision of test specimens for quantitative radiochemical analysis.

1) The test specimens need to be removed from the correct location.
2) Each test specimen needs to be of a uniform and known size.
3) Stringent contamination controls are required to avoid contamination of each test specimen from the hot cell environment, the sampling process and cross contamination between test specimens.
4) Sample management processes must ensure that test specimens are tracked properly throughout the process to avoid mis-identified test specimens.

Inadequate control for the third component, contamination control, is the most common problem which impacts required downstream radiochemical analysis. The following paragraphs will provide background on this critical component.

B. Contamination

There are several possible sources of contamination that can occur in the sampling process. Any contamination of the test specimens prior to and during the sample removal process could invalidate the downstream analyses. Strict contamination controls need to be exercised throughout the sampling evolution and since the potential for contamination always exists, contamination levels need to be monitored. The two major types of contamination issues that can affect downstream analysis are:

- contamination of any species that is to be measured (the analyte), and/or
- contamination by a species that is not being measured, but would complicate down-stream analysis of the analyte(s).

Some types of contamination issues will not affect the results. For example, trace quantities of tin in the sample will not jeopardize the analysis of the ^{135}Cs fission product.

The following paragraphs cover the possible contamination sources, contamination management and methods employed by this experimental program to track potential contamination. This issue is discussed in greater detail in the sections which focus on downstream analysis details.

Many of the analytes being measured for physics irradiation test programs (i.e. fission products and transuranic species) occur in trace amounts in the samples. Thus, they are more susceptible to perturbation by contamination than the sample’s major constituents (i.e. uranium).

1. Contamination Management

Contamination management is a primary concern for all analytical measurements and there are three basic approaches that are employed. Most experimental programs utilize a combination of all three approaches.

a. Avoidance

The best method of contamination management is to not let it happen. Potential contamination can be avoided by structuring the process to be performed in a clean environment and maintaining good housekeeping during the evolution. This includes anything that comes in contact with the test specimen including instruments, chemicals, air, etc. Also the entire process must be considered including storage of the test specimens prior to shipment. The entire process and all components need to be scrutinized from the test specimen's birth to death.

b. Cleaning

If the avoidance method could not be employed and the specimen has experienced some level of contamination, sometimes cleaning methods can be successfully employed. The type of cleaning method is dependent on the sample properties and the type of contaminant. Some components to be sampled can be successfully "cleaned" by wiping down with alcohol. More aggressive methods can be employed such as a dilute acid wash. This method cannot be employed for any component where an acid wash could compromise the sample's structure affecting downstream analysis and/or create procedural problems such as contamination of the reagent (mixed hazardous waste) or the hot cell, or shipment impediment (test specimens must be dry for shipping).

c. Quantification

If the contamination cannot be controlled by the avoidance and housekeeping methods, then there is no alternative except to quantify contamination levels and then subtract the contribution of contamination from the downstream measurements. If good housekeeping is maintained, usually the contamination levels are very small (less than one thousandth of analyte's concentration) with respect to the quantities that are being measured. In these cases, the "blank" correction will be small and will not have a significant effect on the uncertainty of the final results. However, if contamination levels of the species of interest are large with respect to the quantities that are being measured (i.e.greater than 10%), the background corrections contribute to a significant increase in the measurement uncertainty.

2. Potential Contamination Sources

All potential sources of contamination must be considered for the entire process of test specimen removal.

a. Starting Materials

Many of the measured species in these experiments are produced by the fission or activation of uranium, so it is important to know the quantities of the species to be measured in the pre-irradiated components. For example, if neodymium is being measured in the irradiated test specimen, the concentration of neodymium in the sampled components prior to irradiation must be known.

b. Environment

Where and how the components are handled prior to sampling is very important. Radiological controls are maintained wherever irradiated test specimens are processed and radiation levels are typically monitored and controlled. However, some level of contamination always exists. Very often separated components are not protected against potential contamination before they are placed in storage or shipping containers prior to sampling.

c. Materials

Any materials that come into contact with the sampled components and test specimens can contribute to contamination of the test specimen. This includes the reagents used to clean the sampled components, the sample removal tool(s), etc.

d. Processes

The entire process needs to be examined. How is the sampled component removed from the storage container? Where is it placed in the hot cell? How is it cleaned? How is the test specimen removal evolution handled? For example, if the sampled component has been cleaned, but is then picked up by a set of dirty leader follower manipulators, the process has been violated.

3. Contamination Tracking

Even if procedures have been carefully structured and executed to avoid contamination, contamination levels still need to be measured to ensure that the process did not experience any contamination at significant levels. This can be accomplished by analyzing a number of carefully selected blanks. Blank measurements ensure that none of the species being measured is present in the materials used in processing the test specimens. If the species cannot be avoided, blank analyses identify and quantify the amount of contaminant so that a correction can be made to the final result. Blanks can be categorized as reagent blanks and process blanks.

a. Reagent Blanks

A reagent blank is typically a chemical reagent that comes in contact with the sample to be analyzed. No reagent blanks are typically measured for physics irradiation test program test specimen removal since it is not a chemistry process. However, there is an individual component that comes in contact with the test specimen that could introduce potential contamination: the sample removal tool(s). Although these components are not reagents, they provide a single source of contamination and will be treated as a reagent blank.

It is has been documented that small slivers of the sample removal tool end up in the sample containers with the test specimens. This issue needs to be addressed since the condition is not avoidable. For one experiment, a small piece of the sample removal tool was sent to the subcontractor for a complete analysis. The sample removal tool piece was analyzed for the same species of interest that were analyzed for the test specimens. The results showed that no significant amounts (<0.001% of the amount present in the test specimens) of the species of interest were present in the sample removal tool. Thus, slivers of the sample removal tool in with a test specimen would not affect the final results[d].

d. For this case the weight of the small slivers did not perturb the weight of the parent solution, if the slivers were large enough, the quantitative analyses could be affected.

If small slivers of the sample removal tool continue to end up in with the test specimen, then additional pieces of the sample removal tool will need to be analyzed. The analysis of the sample removal tool for one experiment cannot be used as a measure of potential contamination for other experiments. Oftentimes manufacturers change their base materials, process, etc. and this can affect the trace elements in their products. Even high purity chemical reagents can be out of specification and be contaminated. It cannot be assumed that the trace elemental composition of the sample removal tool remains unchanged between manufacturing lots.

b. Process Blank

Measurement of individual reagent blanks are sometimes impractical (and/or costly) especially when dealing with radioactive handling. In the downstream chemistry of the test specimen analysis, composite reagent blanks are frequently used as a “process” blank. The process blank tracks contamination of all the reagents employed in the process, and the process itself. However, if the test specimens were contaminated at the sampling facility prior to shipment, these process blanks would not measure that contamination. Thus a process blank is removed from a non-uranium area of the sampled component. This test specimen experiences the entire process: from when the component was first removed from the irradiated component, through the test specimen removal process, shipping, receiving, dissolution, chemical processing, and instrumental analysis. This process blank is the best measure of the contamination potential for the entire experiment.

III. Sample Characteristics

The very unique characteristics of physics irradiation test program samples make quantitative analyses very challenging. The material composition is the first challenge in the analysis. The major component of the test specimen may not be uranium but another constituent. If uranium is not the major component, it is usually the second most abundant analyte in a test specimen, but may be only 5% of the total test specimen weight. Uranium is one of the easier analytes to measure since it is relatively abundant compared to fission products and transuranic species. The amount of material produced by nuclear reactions is generally very small and is a function of depletion. For a typical physics irradiation test program, the differences among analyte quantities in the least depleted and most depleted test specimens can be as large as three orders of magnitude. The least abundant analyte can be present on the order of ~1 x 10^{-10}% of the total test specimen. Table 1 provides a summary of the measured analyte ranges for a typical physics irradiation test program.

Separation from the major constituents and the variety of other constituents is very tricky for these low abundance analytes. Quantitative measurement of these low abundance analytes is made even more difficult in that the methods typically use carrier free radiochemistry[e] techniques. Since the analytes are present in such small quantities, they are easily lost by adsorbing onto the sides of containers, dropping out of solution with other elements (co-precipitation), ion exchange[f], or via other mechanisms.

e. Radiochemical carrier chemistry can be used for analysis of extremely small traces of an element. In one type of radiochemical carrier chemistry, a weighable quantity of carrier is added to recover the trace element.This technique makes the separation easier, but introduces other sources of errors. More details on this issue can be found in Appendix D.
f. e.g. ^{137}Cs exchanges with potassium in glass and is lost.

Table 1: Expected Analyte Ranges*†

Nuclide	Range (g/test specimen)	Nuclide	Range (g/test specimen)
^{234}U ^{235}U ^{236}U ^{238}U	1 to 9 (x 10^{-4}) 0.1 to 7 (x 10^{-2}) 0.1 to 2 (x 10^{-2}) 0.1 to 1 (x 10^{-3})	^{238}Pu ^{239}Pu ^{240}Pu ^{241}Pu ^{242}Pu	0.0001 to 3 (x 10^{-4}) 0.009 to 7 (x 10^{-5}) 0.002 to 3 (x 10^{-5}) 0.001 to 9 (x 10^{-6}) 0.001 to 1 (x 10^{-5})
^{237}Np	0.03 to 1 (x 10^{-3})	^{241}Am	0.1 to 8 (x 10^{-6})
^{242}Cm ^{244}Cm	0.07 to 2 (x 10^{-11}) 0.2 to 4 (x 10^{-9})	^{99}Tc	0.1 to 1 (x 10^{-3})
^{95}Mo ^{97}Mo	0.4 to 2 (x 10^{-3}) 0.1 to 2 (x 10^{-3})	^{103}Rh	0.6 to 5 (x 10^{-4})
^{101}Ru	0.1 to 1 (x 10^{-3})	^{139}La	0.7 to 3 (x 10^{-3})
^{133}Cs ^{134}Cs ^{135}Cs ^{137}Cs	0.01 to 2 (x 10^{-4}) 0.04 to 2 (x 10^{-5}) 0.1 to 1 (x 10^{-3}) 0.1 to 2 (x 10^{-3})	^{141}Pr	1 to 2 (x 10^{-3})
^{144}Ce	0.02 to 4 (x 10^{-6})	^{147}Pm	~ 1 x 10^{-5}
^{143}Nd ^{144}Nd ^{145}Nd ^{146}Nd	0.1 to 1 (x 10^{-3}) 0.1 to 2 (x 10^{-3}) 0.1 to 1 (x 10^{-3}) 0.09 to 2 (x 10^{-3})	^{147}Sm ^{148}Sm ^{149}Sm ^{150}Sm ^{151}Sm ^{152}Sm ^{154}Sm	0.7 to 5 (x 10^{-4}) 0.4 to 2 (x 10^{-4}) 0.7 to 5 (x 10^{-6}) 0.8 to 2 (x 10^{-4}) 0.1 to 2 (x 10^{-6}) 0.1 to 2 (x 10^{-4}) 0.7 to 4 (x 10^{-5})
^{152}Eu ^{153}Eu ^{154}Eu ^{155}Eu	1 to 7 (x 10^{-8}) 0.1 to 2 (x 10^{-4}) 0.3 to 8 (x 10^{-6}) 0.1 to 2 (x 10^{-6})	^{155}Gd	0.6 to 5 (x 10^{-5})

*. This example pertains to depleted uranium samples that were highly enriched in ^{235}U.
†. Note that test specimens are typically not processed immediately after the end of irradiation: a year or more may have elapsed, thus all short-lived nuclides have decayed. These ranges reflect a large variation in depletion and initial uranium contents.

IV. Process Background

This section provides general background for the analytical techniques employed to process the test specimens. The concept is relatively simple. The test specimen is totally dissolved and taken up into sufficient volume to provide the required aliquots (precisely measured weights or volumes) for each analysis. For most analyses, the element to be measured needs to be separated from the other constituents in the solution and purified prior to measurement. The exact separation and purification methods required are dependent on the analyte to be measured, the quantity of the analyte, the major sample components from which the analyte is to be separated, the measurement technique, and the required measurement's accuracy.

Test specimens are removed from the irradiated component at the central test facility. These test specimens are then shipped to the subcontractor. The subcontractor unloads the test specimens from the shipping cask and transfers the test specimens to a hot-cell to perform the initial dissolution and dilution due to the high radioactivity of the test specimens (which can be as high as 100 REM).

Most test specimens are analyzed for multiple analytes using various techniques. Typically these multiple analyses are performed concurrently by different specialists using different analytical techniques. Thus the experimental process is typically not a sequential process after test specimen dissolution.The following bulleted paragraphs provide an overview of the experimental program and Figure 1 illustrates a generic process flowchart.

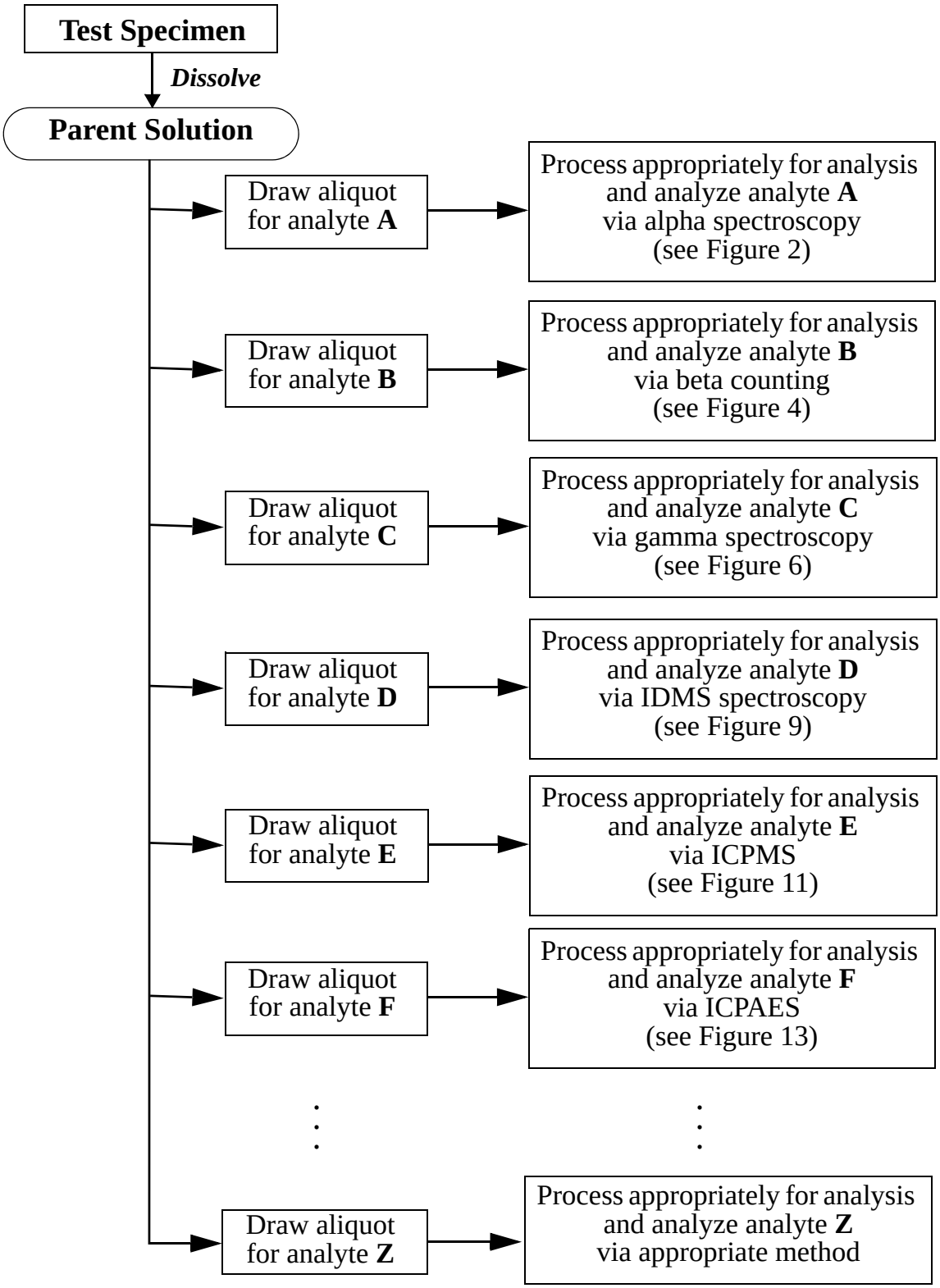
- *Dissolution*: Each test specimen is completely dissolved to get all constituents into solution. This solution is referred to as the "parent solution". Each parent solution is taken up to a similar volume (typically 250 milliliters) and is weighed. This solution provides the needed material for each of the performed analyses. The initial weight of the parent solution is recorded to be used at the end of the analysis to calculate the amount of each measured species in the original test specimen.
- *Aliquoting and Dilution*: The amount of material required for each analysis is dependent on the sensitivity of the analytical method employed for quantitative determinations and the chemical yield of the separation and purification chemistry. A precisely measured aliquot is removed from the parent solution. For most analyses, this aliquot is diluted to provide the appropriate concentration for instrumental analysis. This partitioning and diluting process also allows sample removal from the hot-cell due to the substantially lower radioactivity of the diluted aliquot. The aliquot weight (or volume) and the dilution details are recorded to be used at the end of the analysis to calculate the amount of each measured species in the original test specimen.
- *Addition of Reference Material*: Some techniques require the addition of a precisely measured reference material that serves a variety of purposes in the analysis. The type of reference material used is dictated by the analysis method. Reference materials are covered in Section VIII.A.
- *Chemical Separation and Purification*: Most radiochemical analytical techniques require the analyte to be separated from the other constituents. This isolates the analyte from other species that may interfere in the final measurement. The chemical separation and purification processes appropriate for the analytical measurement technique are designed for each analyte according to its physical and chemical characteristics, the attributes of the constituents it is separated from, and the data requirements.
- *Instrumental Analysis*: Once the analyte is properly processed, the appropriate analytical measurement technique is performed using appropriate instrumentation. The type of instrumental analysis is selected primarily by the analyte's characteristics and data requirements. The data collected by instrumental analysis are then used with information from the upstream evolutions to calculate the total content of the analyte in the test specimen.

The following three sections cover these steps of the overall experimental process in greater detail.

V. Dissolution Process

The primary objective of the dissolution process is to completely dissolve the entire test specimen, without losing any of the analytes. The resulting solution needs to be stable: the analytes need to stay in solution until they are separated. The solution's characteristics should not adversely affect downstream processing. As simple as this sounds, this is where many conditions occur that adversely affect the quantitative analysis of desired analytes.

Figure 1: Generic Process Overview Flowchart



The test specimens may be very difficult to dissolve. The material is designed to remain physically inert in a highly radioactive environment. It is no easy task to completely dissolve the irradiated test specimens. All dissolution methods employed in these experiments involve aggressive acids and/or high temperatures.

The two methods for dissolution of the test specimens are a nitric acid dissolution and a sulfate fusion method. Each method has advantages and disadvantages and it is not the purpose of this document to debate these issues. The following sections provide a general background for each method to provide the reader with sufficient knowledge to follow technical discussions. Additional details on the particulars of these methods (including the advantages and disadvantages of each method) are reviewed in Appendix D.

A. Sulfate Fusion Dissolution

The traditional method for dissolution of these types of test specimens is a sulfate fusion method. In this method, the test specimen is mixed with sodium or potassium pyrosulfate and heated to 1000^{o}C in a furnace. The resulting solid is then dissolved in an appropriate solution (not containing hydrofluoric acid). Additional chemistry needs to be performed to render the solution suitable for downstream processing.

If given a choice, the subcontractor will usually avoid this method due to the use of a high temperature oven in the hot-cell environment and/or due to the sulfate waste issue. However, this procedure is superior when analyzing any species that readily forms insoluble fluorides such as plutonium, neptunium, samarium, and neodymium.

B. Nitric Acid Dissolution

In this method, the test specimen is dissolved in nitric acid solution. A bit of hydrofluoric acid is added to the solution to aid the dissolution and the solution is heated either on a hot plate or via a microwave oven.

This method is simpler than the sulfate fusion dissolution since there is no fusion and there is not as much sample processing required to provide a solution suitable for downstream analysis. However, the addition of too much hydrofluoric acid results in the precipitation of a number of fission products and transuranic species as fluorides.

This type of nitric acid dissolution was successfully used in the large scale plant operations. In this situation, the hydrofluoric acid concentration can be monitored and controlled exactly. It is extremely difficult to control and monitor fluoride concentrations in a sample vial on the bench top.

VI. Radiochemical Separation and Purification Processes

The chemical separation and purification process is dependent on the properties of the analyte, its concentration, the composition of the solution it is being separated from, the analytical measurement technique to be used, what is being measured and the accuracy requirements. Depending on the process, some analytes can be measured as a group, while others need to be completely isolated and measured independently. Often a variety of techniques can be employed to achieve the same end goal. The exact experimental design is left to the expertise of the analytical laboratory performing the work and is dependent on their experience base, capabilities and instrumentation.

This section will provide background on some key experimental processes employed by subcontractors. The following paragraphs cover the experimental evolutions from test specimen dissolution to preparation for instrumental analysis. The intricacies of the chemistry are discussed in detail in Appendix D. Further details on the exact procedures used for each experiment can be found in the subcontractor's documentation (where available).

A. The Care and Feeding of the Parent Solution

Section IV described the creation and weighing of the parent solution. Ideally, the parent solution should remain stable and all constituents should stay in solution for a prolonged time. In reality this typically does not happen. Evaporation of the solution can change its weight (and can result in precipitation of some constituents) affecting the final concentration calculation. Precipitation of some of the constituents can occur the longer the solution sits. Radiation damage can weaken the storage container and result in loss of sample. An acid solution and ultraviolet radiation from fluorescent lamps can age plastic. Over a longer time (1-2 years) plastic bottles can become as brittle as glass and shatter when moved. Leaching of the container can occur which may result in contamination. For these and other reasons, it is very important to process the samples quickly. The longer the solution sits, the probability of something happening that will adversely affect the quantitative process increases. Keeping solutions for later analysis is not a good idea and bottles should never be reused.

One of the common problems in the analysis of transuranics and fission products is precipitation of the analyte. This can be a result of the analyte forming a compound that will drop out of solution and includes polymerization (as is a common occurrence with plutonium) and adsorbtion onto the vessel walls[g]. Co-precipitation can also occur (particularly common for low abundance analytes existing in solution at a level of 10^6 atoms) where the analyte does not form an insoluble compound on its own, but is trapped during the precipitation of another more abundant species in the solution. These issues can happen anytime in the experimental evolution. Co-precipitation is relatively common in the test specimens due to the high concentrations of other constituents[h].

B. Aliquoting and Dilution

The amount of material required for each analysis is dependent on the sensitivity of the analytical technique employed for quantitative determinations and the chemical yield of the separation and purification chemistry. Most of the employed methods can measure less than a microgram of analyte per gram (parts per million (ppm)) of material. For example, the isotope dilution method of measuring uranium by a thermal ionization mass spectrometer needs only a few micrograms[i] of uranium to provide an accurate analysis. Typical test specimens contain tens of milligrams of uranium. Thus the aliquot is further diluted (sometimes by a factor of 1/1,000,000)[j] and a precisely measured portion of the diluted aliquot is sampled. This partitioning and dilution process provides a sample of the proper magnitude for analysis. Dilution often allows for sample removal from the hot-cell due to the substantially lower radioactivity of the diluted aliquot. The aliquot weight (or volume) and the magnitude of the dilutions are required to calculate the quantitative amount of the analyte in the original test specimen.

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g. Also, room dust or lint from clothing can adsorb a significant quantity of atoms.
h. Typically holdback carriers are used to address this issue (see Appendix D for discussion of carriers), however, their use creates a different set of problems.
i. Often only nanograms are required.
j. This is why contamination control is so vital to avoid such small samples from becoming contaminated.

C. Radiochemistry Internal Standard Methods

Internal standards[k] are frequently used in radiochemical analytical techniques for a variety of reasons. These standards are typically added early on in the radiochemical processing and are usually chosen with chemical and physical properties as close as possible to the properties of the analyte. The internal standard will undergo the same loss during the radiochemical processing steps eliminating the need to determine an exact chemical yield (and eliminates the uncertainty associated with determination of exact chemical yield). The internal standard is also used in the downstream instrumental analysis and can be used to determine detector efficiency and account for any instrumental instability during measurements. Additional information on internal standards can be found in Section VIII.A.

A special case of the internal standard method is the method of isotope dilution mass spectrometry (IDMS). This method is based on the determination of the isotopic composition of an element in a mixture of a known quantity of an internal standard (which is called a "spike") with an unknown quantity of the element to be measured. The spike is a solution containing a precisely known concentration of the particular element to be analyzed whose isotopic composition has been changed by enrichment of one of its isotopes. The sample to be analyzed contains an unknown concentration of the element whose isotopic composition is unknown. When a known amount of the sample solution is mixed with a known amount of spike, the isotopic composition of the mixture can be used to calculate the amount of the element in the sample solution. Isotope dilution analysis can be used for all chemical elements that have two or more isotopes, provided that a well characterized, enriched spike is available.

For example, the spike used for the quantitative analysis of uranium is ^{233}U. The NIST[l] spike is over 99.9 atom percent ^{233}U. The samples analyzed for typical physics irradiation test programs contains virtually no ^{233}U[m]. A precisely known quantity of the ^{233}U spike was added to an aliquot of the parent solution which was then radiochemically processed to separate the uranium. Atomic masses were measured via mass spectrometry for each separated uranium sample and are reported as atom ratios. The measured atom ratios were: $^{234}U/^{233}U$, $^{235}U/^{233}U$, $^{236}U/^{233}U$ and $^{238}U/^{233}U$. From these measured ratios and the known mass of added ^{233}U, the quantity of each uranium isotope in the sample was calculated[n]. The advantage of this technique is that addition of the spike prior to radiochemical processing eliminates the necessity of determining exact chemical yields. Comparisons using atom ratios of the measured uranium masses to the spike's major isotope also eliminates the necessity of knowing the efficiency (and stability) of the instrumental analysis. In this example an unspiked sample was not performed. This is because there was essentially no presence of the enriched spike isotope in the sample solution. Normally in isotope dilution, both a spiked and unspiked analysis would be performed since both the sample solution and the spike would contain the same isotope(s).

It is important that the internal standard (or spike) is added as early in the process as possible. Typically the spike is added in a quantity to provide a one-to-one ratio to the most abundant isotope of the measured analyte. It would be beneficial to add the spike to the parent solution. However, three conditions usually discourage this addition: 1) the spike is very expensive and the

k. One type of reference material - see definition on page 30.
l. National Institute for Standards and Technology standard (see Section VIII.A).
m. An unspiked sample solution was analyzed and the test specimens contained less than 0.005% ^{233}U.
n. Some minor corrections were made for the small amounts of isotopes other than ^{233}U in the spike and instrumental corrections.

amount required to be added to these samples (containing milligrams of uranium) would be excessive; 2) if there is a problem with the spike the entire sample is compromised, and 3) if the spike is radioactive it can add too much radioactivity, complicating handling. For the majority of physics irradiation test program measurements, the spike is added to the precisely measured aliquot of the parent solution before dilution. For some species the dilution is performed first to reduce the required quantity of added spike.

D. Separation of the Analyte from the Parent Solution

It is beyond the scope of this document to cover all possible radiochemical methods for the separation and purification of the numerous analytes measured for physics irradiation test programs. Those details can be found in applicable references. This section will provide background on the separation technique most commonly used for physics irradiation test programs which is the ion exchange method. Sample preparation needs to be performed before the ion exchange method can be employed.

1. Sample Preparation for Separation Procedures

Sample preparation for some of the instrumental analytical techniques require the analyte to be separated and purified. The exact separation method is dependent on the analyte, the other constituents in the solution, and the instrumental analytical technique performing the measurement. Many techniques need the analyte to be separated from species that may interfere with the measurement. For example, if uranium is not separated from a plutonium sample being analyzed via mass spectrometry, ^{238}U can interfere with the measurement of ^{238}Pu since they have essentially the same mass[o].

Loss of the analyte through precipitation has already been discussed. However, there are other ways to lose the analyte during processing. Most separations rely on the analyte being in a specific oxidation state. It is possible for a chemical element to exist in solution in different oxidation states. Steps need to be taken to ensure that one hundred percent of the chemical element is in the oxidation state required by the separation method; otherwise losses will occur. It is also imperative that any added spike is in the same oxidation state as the sample. Often the sample solution will be put through several oxidation/reduction steps to be sure the analyte and spike are both in the correct oxidation state. Other processes such as complexing, polymerization, adsorption and volatilization can result in loss of analyte. Details on these processes the can be found in Appendix D.

2. Separation of Analyte by Ion Exchange Method

Ion exchange is a very common method for the separation of chemical elements. It involves the adsorption of a mixture of ions loaded onto an ion-exchange resin followed by selective elution from the resin. There are a variety of specialized resins used in radiochemistry specifically designed for uranium, transuranic species and various fission products.

In ion exchange, the parent solution aliquot is processed according to the requirements of the resin to be used and is loaded onto the ion exchange column. The analyte is preferentially absorbed on the column as all other constituents pass through. The column is then rinsed with a solution which removes the analyte. This is a very simplistic explanation of the process. The analyte has to be in the proper oxidation state and the type and concentration of the loading

o. Provided the measurement is made with a typical mass spectrometer which does not have the required mass resolution necessary to separate the two nuclides.

and eluting solutions are critical. The resin type, column dimensions, and flow rate are also a factor. Often other chemicals need to be added to the solution to make the process more efficient. Some columns will pull more than one analyte out of solution (e.g. uranium and plutonium) and then another separation will be required to separate the individual analytes. Sometimes the additional separation is as easy as washing the column with two different solutions (as in the example for uranium and plutonium) to isolate each analyte. Or it could be more complicated where the solution is passed through another type of column or a different separation technique is used. If a spike was not added to the original aliquot, an internal standard may need to be added to determine the extraction efficiency.

The majority of the radiochemical separations performed in the physics irradiation test programs employ ion exchange methods. The exact details on the methods can be found in the subcontractor's documentation (where available).

E. Physical Preparation for Analysis

Each instrumental analysis requires the samples to be in a specific form. The specific form is dependent on the analyte and the instrumental analysis method employed for each measurement. Some analytes are analyzed as a group and require little preparation. Other analytes require extensive separation and need to be carefully prepared for instrumental analysis. Sample preparation techniques used for the instrumental analysis techniques used for the data collected for the current physics irradiation text programs will be covered in the next section.

VII. Instrumental Analysis

A. Introduction

Selection of the correct technique for instrumental analysis depends upon the characteristics of the analyte, the required data and accuracy requirements. For example, if the analyte is radioactive, radiation detection and measurement can be used. However, this technique cannot be used for stable nuclides. The technique is typically selected by the subcontractor processing the samples. The subcontractors employ three main types of instrumental analysis in the analysis of physics irradiation test specimens as summarized below.

1) *Radiation Detection and Measurement*: gamma spectroscopy, beta counting, and alpha spectroscopy.

2) *Mass Spectroscopy*: isotope dilution mass spectrometry (IDMS) utilizing a thermal ionization mass spectrometer (TIMS), and inductively coupled plasma mass spectrometry (ICPMS).

3) *Atomic Emission Spectroscopy*: inductively coupled plasma atomic emission spectroscopy (ICPAES).

For some analytes, a combination of techniques may be employed.

Table 2 provides the instrumental analysis technique typically used for commonly measured analytes[p]. Some analytes are measured by more than one technique and/or different subcontractors employ different techniques.

p. The table does not provide all possible analysis techniques for each analyte and only lists the techniques typically used to process typical physics irradiation test program samples.

Table 2: Typical Instrumental Techniques for Common Analytes

Analyte	Measured Attribute	Technique
^{234}U, ^{235}U, ^{236}U, ^{238}U	Mass	IDMS or ICPMS
^{237}Np	Alpha energy Mass	Alpha Spectroscopy ICPMS
^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu, ^{242}Pu	Mass	IDMS
^{241}Am	Alpha energy Mass	Alpha Spectroscopy ICPMS
^{242}Cm, ^{244}Cm	Alpha energy	Alpha Spectroscopy
^{95}Mo, ^{97}Mo	Mass	ICPMS
^{99}Tc	Mass Beta emission Optical emission	ICPMS, Beta counting ICPAES
^{101}Ru	Mass	ICPMS
^{103}Rh	Mass	ICPMS
^{133}Cs, ^{135}Cs ^{134}Cs, ^{137}Cs	Mass Gamma energy	ICPMS Gamma Spectroscopy
^{139}La	Mass	ICPMS or ICPAES
^{144}Ce	Gamma energy	Gamma Spectroscopy
^{141}Pr	Mass	ICPMS
^{143}Nd, ^{144}Nd, ^{145}Nd, ^{146}Nd	Mass	IDMS or ICPMS
^{147}Pm	Mass	ICPMS
^{147}Sm, ^{149}Sm, ^{152}Sm $^{144}Sm^{*}$, ^{147}Sm, ^{148}Sm, ^{149}Sm, ^{150}Sm, ^{151}Sm, ^{152}Sm, ^{154}Sm	Mass Mass	ICPMS IDMS
^{152}Eu, ^{154}Eu, ^{155}Eu ^{153}Eu	Gamma energy Mass	Gamma Spectroscopy ICPMS
^{155}Gd	Mass	ICPMS

*. ^{144}Sm is used as a check for Sm contamination since it is not a fission product

The following sections will provide key points of each technique to provide the reader with the necessary background to follow discussions on the individual experimental programs. Additional details can be found in the indicated references for each technique and specific information relating to physics irradiation test program samples are provided in Appendix D.

Please note that instrumental technology is a very fast growing field and dramatic improvements are made each year. Many of the analyses were performed by instruments already outdated by present day standards. It is beyond the scope of this report to document the current cutting edge technology now available in analytical instrumentation.

B. Radiation Detection and Measurement

Radiation measurement techniques employ the principal interactions of radiation with matter as a means of detection. Reference 1 provides additional information on the various nuclear decay processes and details on numerous types of radiation detection and measurements can be found in References 2 and 3.

Radiation can be categorized into two general categories:

1) charged particle radiation (fast electrons and heavy charged particles), and
2) uncharged radiation (electromagnetic radiation and neutrons).

Three sample types of measured radiation for a typical physics irradiation test program are:

1) alpha emitters (heavy charged particle),
2) beta emitters (fast electron), and
3) gamma emitters (electromagnetic radiation).

All the radiation detection and measurement techniques share common elements[q] which are summarized in the following bullets.

- The methods employ the principles of radiation interaction with matter to detect the radiation and to measure the energy distribution of the incident radiation which characterize the measured nuclides.
- Samples need to be properly processed to provide sample mounts with the appropriate geometry for measurement.
- The measured nuclides always behave in accordance with their nuclear characteristics: decay modes, radiations, energies, abundances, half-life, etc.
- The instrumentation requires calibration by well characterized standards.
- Background radiation is characterized and corrected for since the environment and even the materials that make up the detector have natural radiation sources.
- Proper quality assurance programs monitor instrumental operating parameters through use of controls and control chart comparisons.
- Many samples contain multiple radioactive species which have radiation of similar energy. These energy overlaps are resolved by the resolution of the detector, or compensated in other ways such as radiochemical separation from interfering chemical elements.
- Although radiation detection and measurement requires specialized, carefully calibrated and maintained instrumentation, generally the equipment is far less complex and expensive than the other techniques discussed in this report.

The following paragraphs provide the key features that distinguish each radiation spectroscopy technique. Table 3 (page 28) summarizes all the techniques and their attributes.

1. Alpha Spectroscopy

The alpha decay process results in the release of an alpha particle from the nucleus whose atomic number is decreased by two and its mass number by four[r]. The alpha particles from a given nuclide either all have the same energy or are distributed among a few monoenergetic

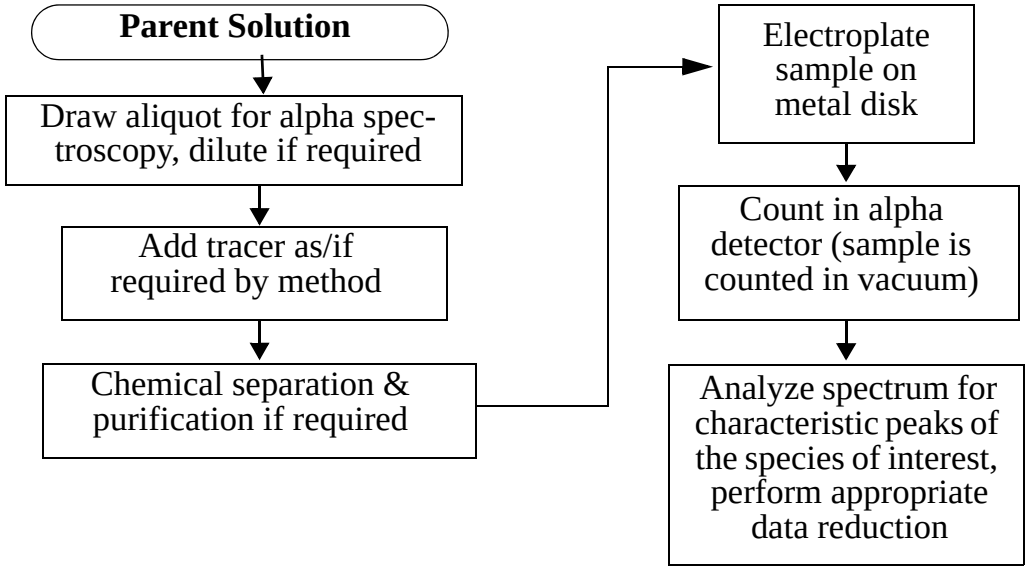
q. Radiation detection and measurement techniques were radiation spectroscopy with the exception of one beta emitter. All attributes common to spectroscopy techniques apply to gross beta counting except for the attributes specific to discrete radiation energies.
r. Decrease of 2 neutrons and 2 protons.

groups. When a single alpha particle energy occurs, the transition takes place to a single energy level (generally the ground state) of the product nucleus. The emission of alpha particles of several different energies by one nuclide occurs when the product nucleus can be left in different states of excitation which subsequently transform to the ground state by gamma emission. Alpha particle energies are limited to between approximately 1.5 to 11.7 MeV.

Alpha particles lose energy very rapidly in materials and must be prepared in very thin layers. Very often nearly weightless sources are needed and achieved by electroplating which requires considerable processing and ensuring that all atoms of the chemical element are in the same oxidation state. Usually tracers[s] need to be employed to provide accurate quantitative analysis, since there is no other method to determine how much of the original radionuclide was recovered. The “weightless” samples are required to ensure that the alpha particles that enter the detector retain almost all of their initial energy. As the sample weight increases, many of the alpha particles lose energy by scattering within the sample causing a much broader energy peak in the detector. This in turn causes overlap with other alpha particles emitted from the sample and makes resolution of one isotope from another very difficult.

Figure 2 provides a generic flowchart for this technique. Specifics on internal standards and/or tracers and chemical processing employed for any given nuclide measured using this technique are dependent upon the analyte, sample composition and the subcontractor’s analysis methods.

Figure 2: Generic Process Flowchart for Alpha Spectroscopy



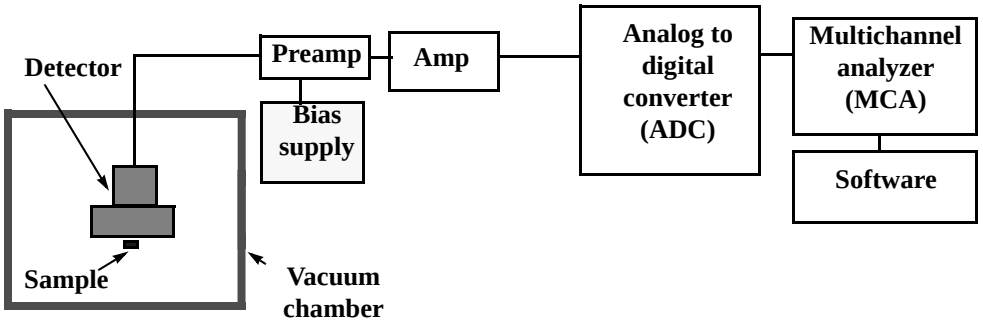
A common detector used for alpha measurement is a silicon charged particle detector which is a semi-conductor diode detector. The window of these detectors are very thin so that alpha particles can enter the active volume and deposit all their energy. The active volume is small because alphas ionize very easily. In addition, the sample and detector is contained within a vacuum chamber to increase detector efficiency (the alphas interacting with the air cannot be

s. Precisely known quantity of a radioactive isotope added to the sample used in quantitative determinations in much the same way as spikes are used.

detected).

The detector's active volume is a depleted region created by placing an applied voltage differential[t] on the detector. When an alpha enters the depleted region, it ionizes the layer. The charge is collected by an applied electric field and generates an electrical signal. The amplitude of this generated electrical signal is proportional to the energy of the incoming alpha particle. A general schematic of this type of detector is provided in Figure 3.

Figure 3: Alpha Spectrometer System Schematic



The signal from the detector then undergoes a chain of signal processing. The first component in the chain is a preamplifier which is located as close as possible to the detector to provide a large signal-to-noise ratio. The preamplifier integrates the charge from the detector and provides a pulse to the amplifier. The preamplifier generally does not provide any pulse shaping functions, but serves to provide a high impedance to the detector to minimize loading while providing a low impedance output to the down line pulse processing components. The resulting product from the preamplifier is rapid rise-time linear pulse of short duration.

The next signal processing component is an amplifier which replicates the original pulse but with amplitude gain. In nuclear application pulse processing, a fast amplifier is typically employed, but only provides an amplitude discrimination at low amplitudes to filter out noise pulses. The analog pulse is converted to a digital input (using an analog to digital converter (ADC)) which is then processed by the multichannel analyzer.

A multichannel analyzer (MCA) is used to measure the differential pulse height spectrum of alpha particles detected by the detector. This analyzer takes the output from the detector via the signal processing chain and sorts the pulse height spectrum as a function of alpha particle energy into bins referred to as channels. However, this pulse height scale must be calibrated to yield absolute alpha particle energy for accurate peak identification.

2. Beta Detection and Measurement

Beta decay is a radioactive decay process in which the mass number of the nucleus remains unchanged, but the atomic number changes. In beta minus decay the atomic number increases by one unit[u], and in beta plus (positron) decay the atomic number decreases by one unit[v]. This can also be accomplished by electron capture which is the capture of an orbital electron. Electron capture takes place most often when a K-shell electron is captured in neutron-

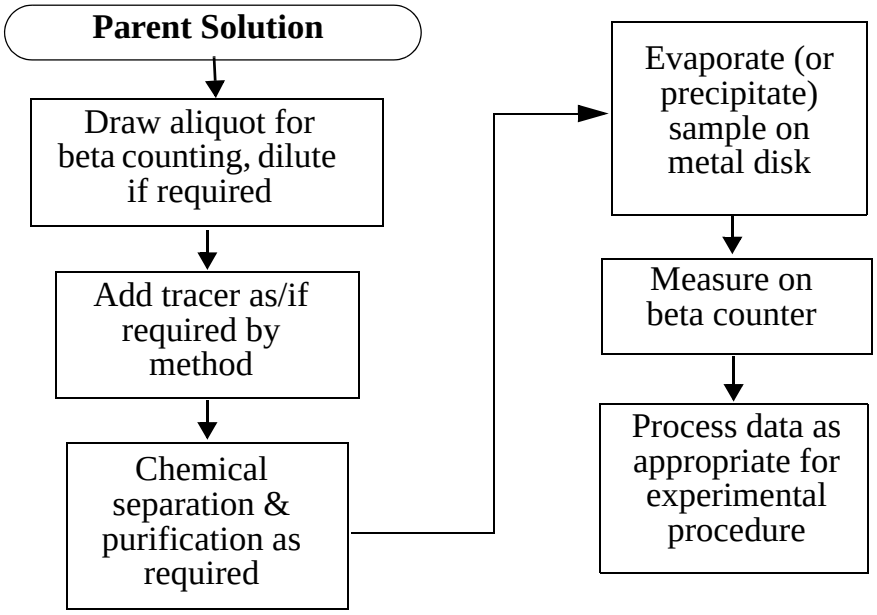
t. This is commonly referred to as "biasing" the detector with the electronic component being labelled as a "bias" supply.
u. Conversion of a neutron to a proton.
v. Conversion of a proton to a neutron.

deficient nuclides. Unlike alpha particles, beta particles do not have unique energies but have an energy continuum. Thus beta spectroscopy is not commonly used for measurement of higher energy beta emitters. Low energy beta emitters, such as ^{3}H and ^{14}C are often counted using a liquid scintillation counting system, which has spectroscopic capabilities.

Complete separation for the beta emitter of interest from all other species is generally required prior to measurement of the gross beta count rate. It should be remembered that there can be cases where there are multiple radioactive species of the same element that decay by beta emission. When this occurs, other methods are needed to assay the radionuclide of interest. Since beta particles readily lose their energy in materials, samples to be counted require preparation in relatively thin layers. Usually tracers need to be employed to provide accurate quantitative analysis.

Figure 4 provides a generic flowchart for this technique. Specifics on internal standards and/or tracers and chemical processing employed for any given nuclide measured using this technique are dependent upon the analyte, sample composition and the subcontractor's analysis methods.

Figure 4: Generic Process Flowchart for Beta Counting

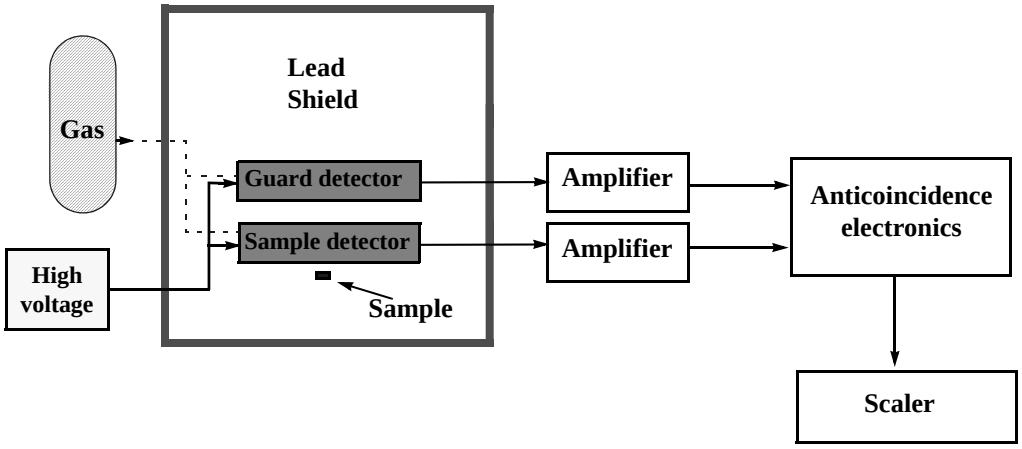


A common detector used for beta counting is a gas flow proportional detector. This detector measures and amplifies the charge resulting from a charged particle passing through a gas. The charged particle enters the gas volume inside the detector and ionizes the gas in a small region near the central wire. The ionization is localized and each primary electron entering the detector produces a small area of ionized gas. The charge is collected at the central wire and a pulse is produced.

As with alpha detectors, beta counters employ extremely thin windows to allow beta particles to enter. The detector background can be appreciable, since it can respond not only to beta particles, but to cosmic rays. Beta counters commonly employ an anticoincidence counting method to reduce the detector background. This counting method will be explained in the following description of the instrument's operation.

Figure 5 provides a schematic of a basic beta counter. The detector assembly consists of two gas flow proportional detectors: the primary (referred to as the sample) detector and the secondary (referred to as the cosmic "guard") detector. The sample is oriented and shielded so that it interacts only in the sample detector. Cosmic radiation will likely penetrate both the sample and guard detectors. The anticoincidence counting electronics discriminates the inputs from the sample and guard detectors so that the output of the sample detector is accepted only when it is not accompanied by a coincident pulse in the guard detector. The pulse is amplified and sent to a scaler. The sample count rate is the total counts minus the background, divided by the count time[w].

Figure 5: Beta Counting System Schematic



3. Gamma Ray Spectroscopy

Alpha or beta decay processes frequently leave the product nucleus in an excited state. Gamma decay results in a change in energy without a change in the atomic or mass number. Gamma radiation is emitted by the excited nuclei transitioning to lower-lying nuclear levels. Because these nuclear states have defined energies, the energies of gamma rays emitted in these transitions are of a specific energy.

Unlike alpha and beta particles, gamma rays do not lose energy rapidly in materials[x] and do not have to be prepared in thin layers[y]. Very often solutions are measured with limited radiochemical processing. Unlike alpha particles which have a limited energy range, gamma radiation can occur over a large energy range: approximately 100 KeV to over 6 MeV. This characteristic allows simultaneous measurement of multiple gamma emitters in the sample provided there are no significant overlaps in gamma ray energies.

Figure 6 provides a generic flowchart for this technique. Specifics on internal standards and/or tracers and chemical processing employed for any given nuclide measured using this technique are dependent upon the analyte, sample composition and the subcontractor's analysis methods.

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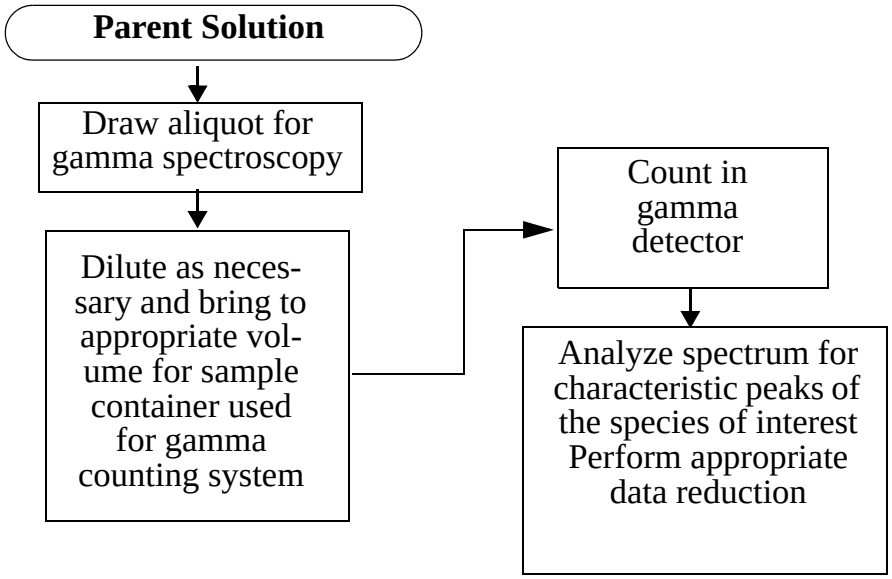
w. The electronics provide time resolution in microseconds, thus there is a measurable dead time that must be accounted for when high level sources are counted (as is the case for all counting methods).

x. Except when attenuated by high Z materials like lead.

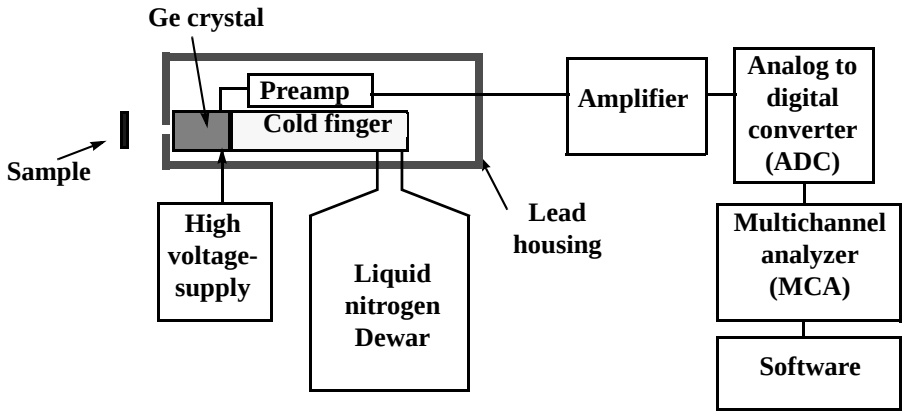
y. Except when measuring low energy gamma rays (i.e. less than 100 KeV).

Figure 6: Generic Process Flowchart for Gamma Spectroscopy



A typical gamma ray spectrometer is comprised of a high purity germanium crystal, liquid nitrogen Dewar, high voltage supply, preamplifier, amplifier, analog to digital converter (ADC)[z] and a multichannel analyzer driven by specialized software as illustrated in Figure 7.

Figure 7: Gamma Spectrometer System Schematic



This schematic looks very similar to the alpha spectrometer schematic since both detectors generate an electrical signal whose signal is proportional to the energy of the incident radiation. Both systems are a type of semiconductor diode detector.

The differences between the detection systems are based on the properties of the two radiation types. Alpha radiation consists of charged particles of about four atomic mass units (amu) in mass and ionize easily. Gamma rays are uncharged, virtually massless and do not ionize easily. Thus a gamma detector does not require a thin window[aa] as required for an alpha

z. New systems now use digital signal processing in place of the amplifier and ADC.
aa. Except for gamma rays less than 100 KeV.

spectrometer. However, the active volume for the gamma spectrometer needs to be larger and of a different composition since gamma rays are not as efficient at ionizing the detector material.

Despite the differences in the two required detectors, the basic operation of both detectors is based on the motion of electron-hole pairs characteristic of a semiconductor. A gamma ray interacts with the detector medium to form a photoelectron which produces electron-hole pairs whose motion in an applied electric field generates an electrical signal. Unlike alpha particle detectors, the high purity germanium crystal requires cooling to maintain structural integrity when high voltage is applied.

The signal processing for gamma spectroscopy is virtually the same as for the alpha detector presented in Section VII.B.1, page 15. A calibration gamma ray source is used to supply peaks of a known energy in the spectrum. The calibration source should have gamma ray energies that are in the same range as those to be measured in the unknown spectrum, since even the best detector system will exhibit nonlinearities of a channel or two over a full range of several thousand channels. It is desirable to have multiple calibration peaks over the range of energies to be measured to provide a more accurate energy calibration.

Data reduction of gamma spectrum needs to be properly executed. For example, multiple isotopes may occur at the same peak and the correct branching ratios[ab] need to be employed. Lawrence Berkeley National Laboratory Isotopes Project has a very handy on-line decay data search for radioactive isotopes where the user can search by nuclide, energy, parent and other attributes (see Reference 4). This search engine is indispensable in finding gamma ray energies and their percentages feeding to daughters, half lives, energy levels, and other data such as atomic data for X-rays and Auger electrons.

C. Mass Spectroscopy Techniques

Mass spectroscopy techniques employ instrumentation designed to separate charged atoms and/or molecules by their mass-to-charge ratio using electrical and/or magnetic fields. Mass spectrometers consist of three essential parts:

1) a source to produce ions from the sample,
2) one or several analyzers to separate the ions according to their mass-to-charge ratio, and
3) a detector to count the ions emerging from the last analyzer and to measure their abundance.

The two mass spectroscopy techniques employed for typical physics irradiation test program samples are thermal ionization mass spectroscopy and inductively coupled plasma mass spectroscopy. The primary difference between these two mass spectroscopy techniques is the source used to produce ions. A general discussion of mass spectrometry instrumentation and principles can be found in Reference 5.

1. Thermal Ionization Mass Spectroscopy

Thermal ionization mass spectroscopy uses thermal ionization for ion production. The instrumentation is designed to generate and analyze positive ions since most elements produce positive ions more readily than negative ions. Also, positive ions typically produce more stable ion beams.

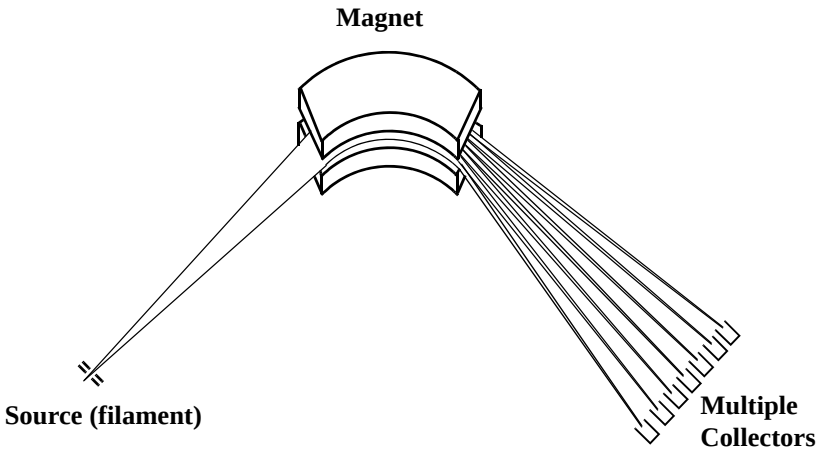
ab. Branching ratio is the ratio between decay rates of the different decay modes for the process.

Thermal ionization mass spectroscopy requires the sample to be a single chemical element, highly purified, and usually in a specific chemical form to provide efficient ion conversion and stable ion beams. Tiny amounts of liquid sample are evaporated upon a thin ribbon filament that is heated to hundreds of degrees which facilitates evaporation and ionization. The chemical form of the sample, the type of filament, and the temperature is dependent on the chemical element being measured. The filament serves to atomize and ionize the sample. During atomization, a process known as mass fractionation occurs. For a given chemical element, heavier atoms require more energy to be atomized and ionized than lighter atoms. Thus, ions for the lighter isotope of a chemical element are more readily produced than the heavier isotopes. Mass fractionation is typically measured using a NIST isotopic standard. Mass fractionation per mass unit is calculated and the final data are corrected. Mass fractionation values are a function of the chemical element, filament type, chemical form, and instrumentation. They can vary with time and must be measured for each analysis set.

It is essential that any mass interferences are eliminated. Isobaric[ac] interferences or molecular[ad] interferences can exist at the same mass as the measured nuclide and provide erroneous results. Thus one of the primary difficulties with these methods is complete separation of the chemical element to be analyzed from all other constituents to avoid mass interferences.

The instruments used for physics irradiation test program measurements were single magnetic sector instruments where a magnetic field was used to separate the ions according to their mass-to-charge ratio. The employed detection systems were multiple collector systems where the detectors are spaced on the magnetic focal plane to measure each mass simultaneously as illustrated in Figure 8.

Figure 8: Multiple Collector Magnetic Sector Mass Spectrometer Schematic



Multiple collector systems have several advantages to single collector systems where the magnetic field is switched to measure each mass sequentially. Some advantages of multiple collector systems are described as follows.

- Multiple collector systems are not as susceptible to variations in the source current since all masses are measured simultaneously.

ac. Isotopes of different elements with the same mass.

ad. The molecular interference is a combination of two or more species (i.e. $^{90}Zr_2$, at mass 180; $^{238}U^{16}O$ at mass 254;$^{176}Hf^{1}H$ at mass 177) and does not need to be chemically stable to be detected by the instrument.

- Data acquisition is faster since multiple masses are measured simultaneously and there is no wait necessary for stabilization of the magnetic field since the magnetic field is held constant.

Multiple collector systems are not without some disadvantages when compared to single collector instruments. Some disadvantages are summarized below.

- The systems are more expensive and difficult to maintain.
- Since the currents are measured by different detectors, the efficiency of each detector needs to be carefully determined and the data needs to be properly corrected for the bias between the detectors and a reference voltage.
- Multiple collector systems generally employ analog detectors which do not provide the sensitivity of pulse counting systems for the measurement of very small samples (picogram quantities).

The type of detector most commonly employed in the multiple collection instruments is a Faraday cup. A Faraday cup is an analog device that measures the ion current bombarding the detector. The current is converted to a voltage using a high precision resistor and the raw data are reported as atom ratios according to the software[ae]. The majority of measurements employed an isotope dilution technique (see Section VI.C, page 11 for more details). The combination of the isotope dilution method using thermal ionization mass spectrometry as the measurement technique is known as isotope dilution mass spectrometry. Figure 9 provides a generic flowchart for isotope dilution mass spectrometry. Specifics on spikes and chemical processing employed for any given nuclide measured using this technique can be found in the reports which detail each physics irradiation test program experiment.

Thermal ionization mass spectrometers are expensive, a challenge to maintain and operate, sample preparation is generally very extensive, and many calculations are required to provide end data. However, IDMS still provides the most accurate and complete quantitative analysis of all mass spectrometric techniques. This may not be the case in the future, as technological advances provide inductively couple plasma mass spectrometer (ICPMS) instrumentation with increased capabilities that could eventually match and even exceed other analytical techniques.

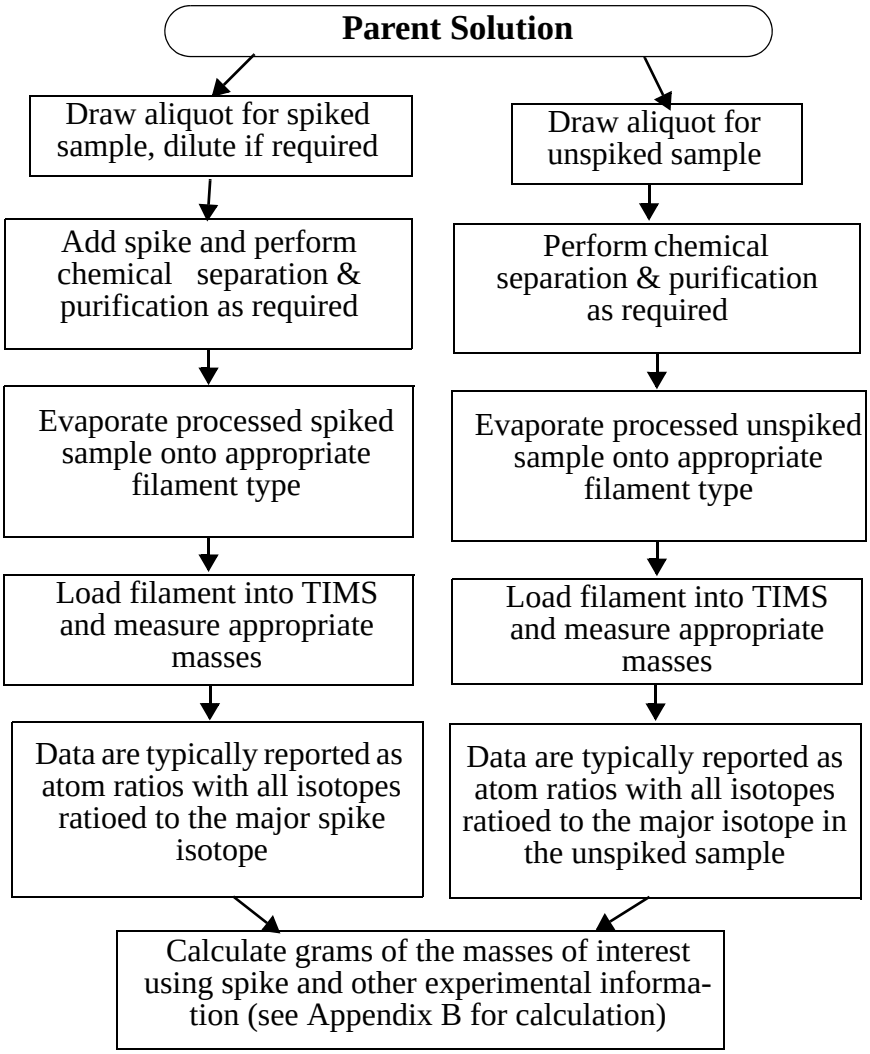
2. Inductively Coupled Plasma Mass Spectroscopy

Inductively coupled plasma mass spectroscopy is a relatively new[af] technique that only recently has been applied to high accuracy quantitative isotopic measurements. Although potentially less accurate than TIMS, ICPMS has the advantage of allowing analysis of mixed samples, thus greatly simplifying the preparatory radiochemistry. ICPMS was initially developed to provide ultra-trace elemental analysis of metals, soils and water. New generation ICPMS instruments employ high resolution magnetic sector analyzers and pulse counting detectors. ICPMS instruments employing dynamic reaction cells can be used to reduce the amount of sample preparation time and eliminate a number of interferences. Some laboratories have replaced their other instruments with high capability ICPMS instruments.

The following discussion is specific to the processing of physics irradiated test program samples. The instruments used to collect data for recent experiments were older models with none of the new technological improvements. The basic function of ICPMS is similar to TIMS with different components executing each of the three basic mass spectrometry

ae. The denominator of the ratio is usually the spike mass or the major isotope.
af. When compared to other techniques.

Figure 9: Generic Process Flowchart for Isotope Dilution Mass Spectrometry



functions as summarized on page 21. The ICPMS instrument used for the analysis of physics irradiation test program samples was a quadrapole instrument and a basic schematic is provided in Figure 10.

ICPMS uses a plasma for ion production and, as with TIMS instruments, positive ions are produced and measured for each analyte. The plasma source derives energy supplied by electrical currents which are produced by time-varying magnetic fields (induction). The ion signal depends on a large number of instrumental parameters associated with the plasma (torch geometry, gas flow rates, gas composition, generator power and frequency) and sample introduction. The plasma source is more complicated than the relatively simple TIMS source and discussion of the ICPMS source components and physics is beyond the scope of this report. Additional details can be found in Reference 6.

The sample solution may have undergone some radiochemical processing prior to ICPMS analysis. Figure 11 provides a generic flowchart for this technique. Specifics on internal standards and/or tracers and chemical processing employed for any given nuclide measured

Figure 10: Basic Inductively Coupled Plasma Mass Spectrometer Schematic

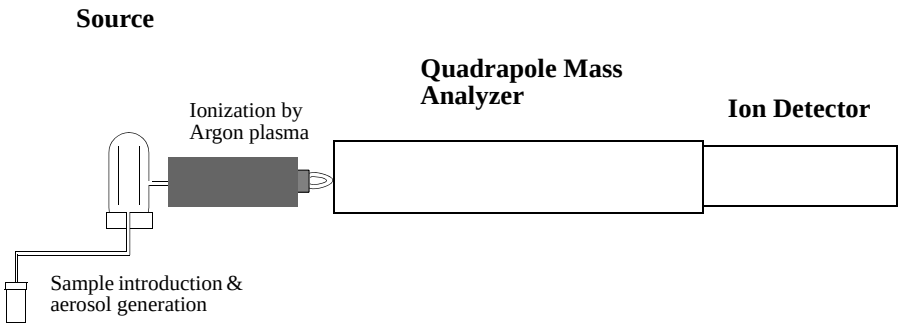
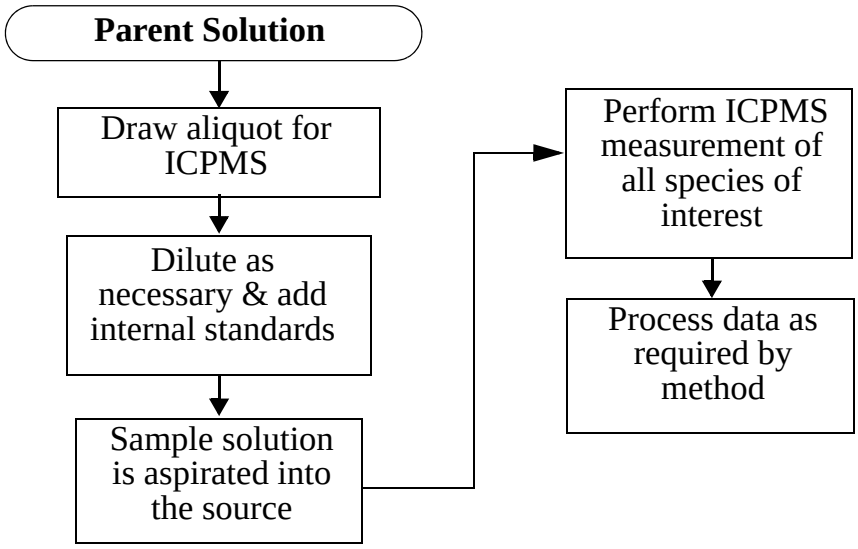


Figure 11: Generic Process Flowchart for Inductively Coupled Plasma Mass Spectroscopy



using this technique can be found in documentation which details individual experiments. Internal standards were always added to the sample to not only provide quantitative results, but also compensate for matrix effects and inherent instrumental drift. The sample solution was then aspirated into a high temperature (thousands of degrees) argon plasma which atomized and ionized the sample.

The ion beam then traveled into the mass analyzer that separates ions according to their mass-to-charge ratio. Mass-to-charge separation was achieved using a quadrapole mass analyzer. The quadrapole uses the stability of trajectories in oscillating electric fields to separate ions according to their mass-to-charge ratio. Quadrapole mass analyzers are popular on ICPMS instruments since they are simple, inexpensive, and provide good performance. However, their disadvantage is they have low mass resolution and data collection is sequential as with any single collector instrument.

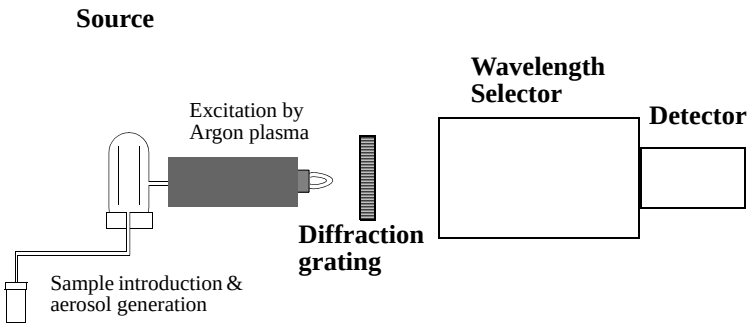
The type of ICPMS detector used to measure data for physics irradiation test programs was an electron multiplier. An electron multiplier is a device that multiplies an electronic current by accelerating the electrons on the surface of an electrode. The ion strikes the first electrode (which is at high voltage) and electrons are released by the impact. The collision yields a number of secondary electrons higher than the number of incident electrons, the secondary electrons are accelerated towards another electrode which in turn gives off additional secondary electrons, and so on through the number of electrodes in the electron multiplier. In this way the signal is "multiplied" and a single ion generates a measurable pulse. ICPMS instruments have a large dynamic range meaning that the signal magnitude to be detected is in the range of 0.1 ions/second for ultratrace components and up to 10^{10} ions/second for major components. For low signals ($<10^6$ ions/second), an ion-counting system is usually employed, while for higher signals some form of analog measurement is used. Electron multipliers can provide detection over the entire dynamic range since they can be operated in both ion counting mode and analog mode. For analog mode, the high voltage applied to the secondary electron multiplier is reduced, lowering the detector's gain when measuring major components.

The advantage of the ICPMS method is the ability to simultaneously measure isotopes for over a dozen elements with little radiochemical processing[ag]. This can dramatically reduce the cost of a physics irradiation test program. However, some species suffered mass overlaps and separation radiochemistry was employed to provide more accurate data.

D. Inductively Coupled Plasma Atomic Emission Spectroscopy

Inductively coupled plasma atomic emission spectroscopy (ICPAES) uses quantitative measurement of the optical emission from excited atoms/ions to determine analyte concentration. The front end of the ICPAES[ah] is similar to an ICPMS where the major components are the sample introduction system (nebulizer), the ICP torch, high frequency generator, and transfer optics. A basic schematic for a basic ICPAES provided in Figure 12.

Figure 12: Inductively Coupled Plasma Atomic Emission Spectrometer Schematic



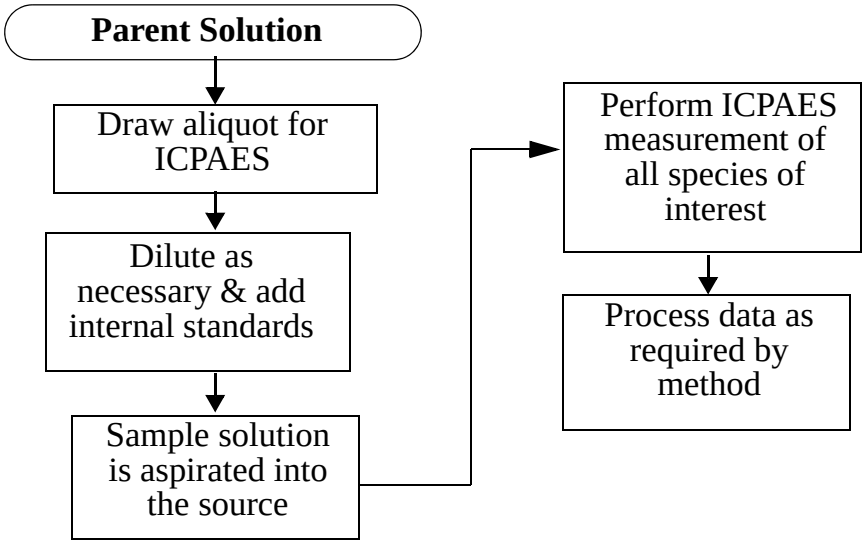
The analyte is dissolved in a solution and aspirated into the plasma (excitation source) which ionizes the atoms. In the process, the atoms/ions are promoted to high energy levels. The atoms/ions decay back to lower levels by emitting light. The light is resolved into its component

ag. Quicker analysis times: a few minutes for each sample.
ah. Also it can be described as an optical emission spectrometer (ICPOES).

radiation by means of a diffraction grating and the light intensity converted to an electrical signal with a photomultiplier tube at the specific wavelength for each element line. The desired wavelength is selected using some type of wavelength selector, typically a monochromator or polychromator. Each element will have many lines in the spectrum which can be used for analysis. The selection of the best line for analytical determination requires experience and is dependent on the other species present in the solution, including the major sample components. The intensity of the electrical signal at the specified wavelength for the analyte is compared to previously measured intensities of known concentrations of the analyte and a concentration is computed. The most common ICPAES employed to collect data for physics irradiation test programs has a polychromator spectrometer which is a simultaneous instrument where all lines are measured at the same time (similar to a multiple collector mass spectrometer).

Figure 13 provides a generic flowchart for this technique. Specifics on internal standards and/or tracers and chemical processing employed for any given nuclide measured using this technique can be found in documentation which details individual experiments.

Figure 13: Generic Process Flowchart for ICPAES



AES techniques are generally used for chemical elemental analysis only since the optical emission is not specific for individual isotopes of a chemical element. However, AES techniques can be used to measure mono-isotopic analytes and can be employed with another measurement method to produce results for specific isotopes of a chemical element. This method has not been extensively utilized in physics irradiation test programs. Additional details on ICPAES can be found in Reference 7.

E. Summary

This chapter provided a brief overview of the instrumental analytical techniques for background purposes and these techniques are summarized in Table 3. The discussions in this chapter did not provide the intricacies of each method and the level of work required to produce correct data. Additional details on each technique can be found in Appendix D.

Table 3: Summary of Instrumental Analysis Techniques

Experiment	Sample Set	Sample Form	Measured Attribute	Source/ Excitation Method	Separation Method	Detector
Radiation Detection and Measurement	Alpha emitter	Near "weightless" sample electroplated on metal disk or co-precipitate	Alpha particle count rates as a function of energy	The sample itself	Multi-channel analyzer Semi-conductor surface barrier detector	
	Beta emitter	Sample evaporated on metal disk	Gross beta particle count rates	The sample itself	Proportional counter (gas-filled detector)	
	Gamma emitter	Solution or solid sample	Gamma ray count rates as a function of energy	The sample itself	Multi-channel analyzer Semiconductor (solid-state) germanium detector	
Thermal Ionization Mass Spectrometer	Stable or radioactive element	Solution dried on filament	Ions as a function of their mass to charge ratio	Thermal ionization	Magnetic sector mass spectrometer	Faraday cups (voltage) or electron multiplier
Inductively Coupled Plasma Mass Spectrometer	Stable or radioactive element	Solution	Ions as a function of their mass to charge ratio	Plasma	Quadrapole mass spectrometer	Electron multiplier
Inductively Coupled Plasma Atomic Emission Spectrometer	Chemical element or mono-isotopic element	Solution	Emission lines from atoms/ ions decaying from excited energy levels	Plasma	High-resolution polychromator	

VIII. Quality Control for Radiochemical Analytical Laboratories

Physics irradiation test programs required that all analyses are performed to the best possible quality by the available techniques. The required attributes of the subcontracting laboratory is that they had the competence to perform the work, suitable facilities and equipment, and maintained good laboratory and measurement practices. The subcontractor needed to have adequate quality control of all their processes used in the analysis for each experimental program, a method to evaluate their ability to maintain adequate quality control, and provide the proper documentation. Quality control is defined as those operations that ensure that the produced data are generated within known probability limits of accuracy and precision[ai]. Quality control programs are designed and are specific for each process. These programs are structured by what needs to be measured and how well, the measurement processes, and what needs to be done to obtain reliable measurements. All reputable analytical laboratories maintain a quality assurance program which

ai. Accuracy and precision are characteristics of actual measurement process. Typically, the true accuracy and precision are not known exactly, but are estimated. "Confidence" refers to the level of certainty with which the accuracy and precision are estimated. See Appendix C and References 9, 10, 11 for additional details.

is designed to assure clients that the laboratory is generating data of a proven and known quality. Quality assurance programs depend primarily on documentation which provides information on key quality assurance processes such as quality control operations, accountability of data, traceability of reported data and avoidance of any falsification of data.

The principles of quality control and construction of quality assurance programs is beyond the scope of this report. An excellent treatise on this topic can be found in Reference 8 and some additional quality control details specific to physics irradiation test programs are provided in Appendix D. However, the reader should be familiar with some of the key quality assurance components and how they affect the level of confidence in the experimental results.

Some key components of quality control are:

- sample management (sample and sub-sample control to maintain sample integrity and proper identification),
- instrument calibration and control charts (to ensure instruments are properly calibrated and remain in calibration),
- reference materials (used for calibration and to assess the measurement method),
- blanks (to monitor contamination from all sources external to the sample), and
- documentation (control charts, instrument logs, laboratory notebooks that include written down observations).

Additional details for two key quality control components (references and blanks) will be helpful prior to discussion of qualitity control evolutions. The following sections only cover the types of reference materials and experimental blanks used in typical physics irradiation test programs[aj].

A. Reference Materials

Well characterized reference materials are key to the accuracy of quantitative analysis. There are generally two categories of reference materials: elemental and isotopic. Elemental references are typically solids of a known chemical elemental composition which can be precisely weighed and then dissolved to provide standard solutions of a known concentration. Isotopic standards are typically composed of a single chemical element with well characterized isotopic abundances. Some isotopic standards usually can be procured in a variety of different isotopic abundances for the same chemical element. Most reference standards are purchased from the National Institute for Standards and Technology (NIST), although some laboratories also manufacture reference standards that are carefully cross checked against NIST materials. The following paragraphs provide typical definitions for the major reference material categories.

- *Calibration Standards:* These standards are primarily used as an external standard to calibrate instrumentation for analytical measurements and are sometimes used as references for control charts.They ensure that the instruments are operating properly and are measuring the correct entities such as the correct gamma ray energy, the correct mass, etc.
- *Control Standards:* These standards will typically be selected to cover the range of analyte(s) to be measured. For example, the calibration standard used to calculate the energy calibration curve for a gamma ray spectrometer will be composed of the isotopes that cover the entire energy range that will be measured. These standards are typically tracked on control charts. These standards correct instrumental characteristics but provide no check of the chemistry.

aj. This is not an inclusive list of reference materials and blank types used in the examination program.

Often laboratories will fabricate in-house control standards. These control standards will match the characteristics of the samples to be analyzed as closely as possible, be analyzed using the same method to be employed for the samples to be analyzed, and are characterized using calibration standard(s) and frequently are tracked on control charts. These customized controls are very useful since a NIST standard with the same characteristics as a real world sample is rare to find. Such standards are defined as "secondary standards" since they are calibrated against primary standards[ak]. For example, if uranium isotopic abundances of the analyzed samples fall outside of the available uranium isotopic standards, a suite of controls will be created that cover the range of expected uranium isotopic abundances of the samples to be analyzed. These standards typically provide a check of the equipment[al].

- *Internal Standards:* These standards are used for the internal standard technique which is based on comparison of the signal corresponding to the analyte to be quantified with that of a reference called the internal standard. This technique allows the elimination of various error sources other than the intrinsic error due to counting statistics.

  For example, thallium is added to samples to be measured via ICPMS to correct for instrumental instabilities. These standards also can provide a check of both the equipment and the chemistry. Note that the definition of "internal standard" can be defined differently, dependent on point of view. The example for ICPMS was already provided and represents a chemistry and instrumental point of view. However, an instrumental scientist may view internal standards as standards internal in the instrument such as a reference voltage used to calibrate multiple detectors.

- *Cold References:* These references[am] are unirradiated samples of the experimental specimens that were irradiated. Analysis of these samples provide the pre-irradiation information which is key in determining uranium depletion and fission product and transuranic build-up.

Quantitative analysis is only as good as the reference materials used in the experiment. The reference materials must be handled properly (not contaminated or inadvertently diluted or concentrated) and verified at regular intervals. Good scientists typically employ a suite of various reference materials to characterize their methods and instrumentation and to verify experimental parameters such as chemical recovery. Selection of reference materials is dependent upon a variety of factors: the characteristic and concentration of the analyte, the starting matrix, sample processing methods, the performed analytical measurements, and the required accuracy.

B. Blanks

Blanks fall into a more general category of "background", which is nomenclature used predominantly in radiation detection techniques. In those techniques, the inherent radiation background in the counting laboratory needs to be measured and subtracted from the analyzed sample. In radiochemical analytical analysis, monitoring background levels is typically more complicated, and a variety of blanks are employed. There are many opportunities for contamination of the samples from the reagents, labware, the environment the analysis is performed in, and by the analyst performing the analysis. It is imperative to be proactive and develop procedures to reduce

ak. See Appendix D for an explanation of primary and secondary standards.

al. They can also be employed to provide a good check of the chemistry if they are processed via the same process as the samples and then measured using the same technique. However, in this application it is no longer a control standard but a process spike that checks the chemistry.

am. It is imperative to have a good paper trail and record keeping on these references because it may be years before this cold reference data is used.

the possibility of contamination. These procedures include, but are not limited to, controlling the experimental environment, cleaning of labware, use of high purity reagents and careful handling of samples.

The topic of contamination and its management was introduced in Section II.B and that information will not be repeated here. However, there is some additional information on blanks when discussing radiochemical analysis. All blanks relating to the radiochemical analyses commonly used in physics irradiation test programs are summarized in the following paragraphs.

- *Reagent Blanks:* These blanks are comprised of a single reagent used in the radiochemical processing. They are typically performed any time there is a new bottle of reagent. The analysis is performed prior to the reagents' use to avoid contamination of the actual samples.
- *Composite Reagent Blanks:* Very often laboratories will run composite reagent blanks that are comprised of all the reagents used to process the actual samples. This is more efficient than analyzing individual reagents provided that the laboratory has good quality control and a reliable supplier. However, if the composite reagent blanks are contaminated, then individual reagent blanks will need to be analyzed to pinpoint the contaminated reagent(s) (or discover that the contaminant is in the environment or the labware).
- *Process Blanks:* These blanks are comprised of the major components of the actual samples and all of the reagents used to process the actual samples. These blanks are performed in parallel with the actual samples and are only valid as blanks for the samples that they are run with. They track every process that occurs to the actual samples in the same environment and in the same type of labware. The reagents are added in the same quantity and time as they are added to the actual samples. Note that a blank only applies to the set of samples run with the blank. Blanks are control charted to look for trends, but a blank cannot be used for a different batch of samples.
- *"True" Blanks:* These are blanks that contain everything that is in the actual sample except for the analyte. It is very rare that this type of blank is available for a given sample and particularly difficult for irradiated samples. The closest sample to a "true" blank for these experiments were test specimens removed from an area composed of all constituents except for uranium to provide an overall process blank. This blank not only accounts for contamination during the radiochemical processing at the subcontracting laboratory, but also the sample removal processing and packaging in the production hot-cells.

Appropriate blanks are key to the quality assurance program of any experiment. The type and number is dependent upon the process and required quality assurance. It is also important to have a variety of different types of blanks to pinpoint the contamination source if any are found. Once the contamination source is found and corrected, the analysis can be repeated on another aliquot of the parent solution for cases where the parent solution has not been contaminated. If the parent solution is contaminated, then that sample is compromised and is of limited use. For example, if the parent solution was contaminated with plutonium, the solution could still be used for other analyses. Or if the contamination was small and could be quantified, the data could be corrected for the contamination. However, the uncertainty of that measurement would increase due to the uncertainty associated with the contamination measurement.

Note that there is rarely a "zero" blank. There is almost always a background of any given analyte. Typically the contamination level is orders of magnitude below the sample levels. This needs to be confirmed by quantitatively analyzing the contamination so that the appropriate blank corrections can be performed if needed. Note that larger blank corrections increase the uncertainty in the final measurement.

C. Application

It is very difficult to provide a generic outline of a quality control program for a complex experiment since it is composed of many different processes dependent on what is being measured and how it is being measured. However, the terms defined in the previous two sections are difficult to grasp without an example of how they interrelate in the overall quality assurance program. This section will attempt to provide a process description of the quality control program by presenting a general overview of important quality control components, where and how they are used, and why. Additional details can be found in Appendix D.

It may help the reader if they keep in mind that the quality control issues for a radiochemical analysis are conceptually no different than engineering quality control issues. Consider the design and manufacturing of a nuclear reactor as an example. Everything that goes into that reactor and everything that is used to verify what goes into that reactor has a quality control plan. So whether it is a material that is used to manufacture a reactor component, or the computer code that is used to calculate important parameters, test cases using standards where the answer is already known are used to determine the quality of what is being produced/measured. If the correct answer is not obtained, there is something wrong and it needs to be investigated. A chemistry quality control plan accomplishes the same goal using similar concepts (calibration standards, verification of composition, process checks, etc.) - only some nomenclature may differ.

One approach to explain the quality control issues involved in a complex radiochemical analytical analysis is to break the process into four main categories. Practically all radiochemical analytical techniques can be broken down into these four categories[an] which can then be individually explained to provide a coherent overview of typical radiochemistry quality control issues.

- *Equipment:* The equipment (i.e. ion exchange columns) and analytical instrumentation (i.e. gamma spectrometer) used to process and/or analyze the samples must be working properly. Equipment needs to be checked prior to starting the sample analysis
- *Background*: There can be no unmeasured contributions of the species being measured from the environment. The environment is defined by the type of analysis. It may be the gamma ray background for gamma spectroscopy, trace impurities in chemicals used for sample dissolution, or a contamination in the hot-cell where the sample is being processed.
- *Standards*: The majority of analytical procedures require the use of some sort of standard. These standards may be simple elemental internal standards added for monitoring instrumental stability during the instrumental analysis, or be precise quantities of high purity reference material added to the solution for accurate quantitative analysis.
- *Chemistry*: All chemical procedures (i.e. dissolution, separation, etc.) must be working properly and adhered to throughout the process.

The individual components relative to the experimental method should be investigated immediately preceding the analysis of the samples to demonstrate that the process is working properly. If any issues are revealed during these investigations, the situation can be remedied and verified before wasting resources on sample processing. These extremely important investigations cannot be omitted. Most analyzed samples are one-of-a-kind samples and if there is an unrecoverable analysis error, the information is lost. These evolutions are similar to the verification of material prior to component manufacturing, verification of components prior to assembly, calibration of measuring equipment, etc.

Table 4 provides examples of commonly employed quality control checks for each of the four main categories. Note that some quality control techniques can be used to check more than one of the four

an. A fifth category of data reduction is not included here since it is not as unique as the radiochemical & instrumental analysis issues.

categories. For example, verification of the composition of a standard checks both the composition of the standard and the functionality of the instrument used to perform the analysis. All is well if the analysis agrees with the recorded composition of the standard. However, if there is a disagreement, the problem can be with the standard, the instrument used to analyze the standard, or both. Troubleshooting experimental problems is sometimes not a straightforward issue.

Table 4: Examples of Typical Quality Control Evolutions for Sample Analysis

Check	Process	Why Performed	When Performed
Equipment Background	Instrument calibration	•Calibrates and establishes the properties of the instrument: is the data being collected at the correct energy? the correct mass? What is the detector efficiency? etc.Example: energy calibration for a gamma spectrometer.	•Depends on instrumentation: typically at least once a year; whenever any change is made; an instrumental problem is suspected; or an instrumental problem has been corrected.
	Instrumentation check out using control standard	•Some laboratories will use control standards that are more similar to the sample to be analyzed. •For example, some laboratories routinely use a combined cesium and cobalt source to calibrate and check out their gamma spectrometer. The source measurements are often plotted on a control chart which tracks the instrument's performance as a function of time. If a sample containing a mixture of fission products is to be analyzed, the laboratory will sometimes use a mixed fission standard for instrument calibration and check-out.	•Periodically, depends on the instrumentation. For example: counting techniques typically will run a control sample once a week. Many TIMS facilities will run a control sample once a day. •In some laboratories, specialized in-house fabricated control samples are frequently run prior to sample analysis with a periodic check if the experiment is performed over a longer time period. This is done to ensure that the instrument is operating properly prior to analysis of one-of-a-kind samples.
	Addition of an internal standard to the sample	•This internal standard is to monitor the instrument stability during the instrumental analysis. This type of standard is very important for ICPMS analysis.	•Added to the sample prior to instrumental analysis.
Background	Run instrument with no sample or with a blank sample. Example: deionized water in a sample container for gamma spectrometry (provides shielding)	•To measure background contribution from the environment of the species to be analyzed. •For example, a background for an alpha detector would be to run an overnight count with an empty sample holder inserted in the instrument. The reason to include the sample holder is in case there are any alpha emitters in the sample holder material.	•Periodically depends on the instrumentation. For example: counting techniques typically will run a background once a week.
	Analyze reagent blank(s)	•Determines that the reagents do not contain any appreciable* amount of the analyte being measured. •For example, if uranium and plutonium are to be measured, the amount of uranium and plutonium will be analyzed in this reagent(s). Even though laboratories use high purity chemicals in their procedures it is not impossible to receive a contaminated reagent from a manufacturer or have an existing reagent bottle contaminated by a careless chemist.	•Prior to use of the reagents •Note that each bottle may need to be tested since it cannot be assumed that bottles from the same manufacture are equivalent.
	Process composite reagent blank using the same process and equipment that will be employed for the samples	•Determines if the entire process (i.e. reagents, labware, environment, instrumentation) is free of species that may perturb the results. •Typically laboratories who have a high confidence in their cleanliness will use this approach in place of individual reagents blanks and other checks (i.e. perform and analyze swipes of laboratory surfaces).	•Typically processed concurrently with the actual samples. •Note that it is sometimes impossible to eliminate all traces of a certain element. In those cases it is imperative to run a process blank in tandem with the samples to provide a quantitative measurement which is then used to blank correct the final analysis.

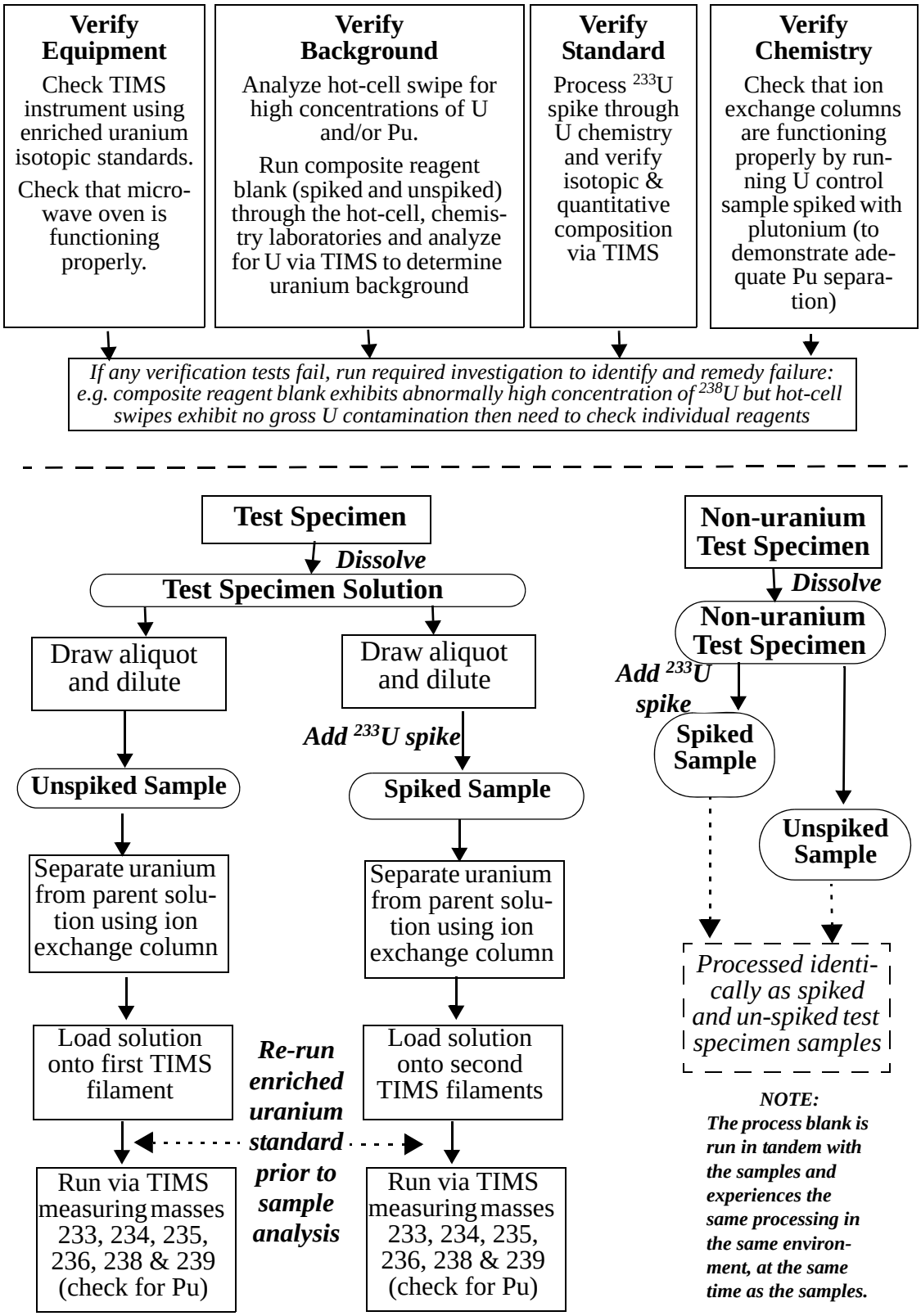
Table 4: Examples of Typical Quality Control Evolutions for Sample Analysis (Continued)

Check	Process	Why Performed	When Performed
Back-ground *continued*	Run a "process" blank in tandem with the actual samples	•To measure the amount of the measured species that does not originate in the sample. •The process blank used in the majority of the experiments documented by this report were test specimens from the non-uranium bearing regions. •Blanks were very important to the experiments documented in this report since many of the analytes to be measured were processed for other samples in the same laboratory (i.e. on facility processed large amounts of plutonium and uranium in their hot-cells where the test specimens were dissolved, diluted and aliquoted).	• The process blank follows the same exact evolutions as the samples, the same amount (from the same bottles) of reagents were added, the same internal standards (if used) were added, the same chemistry was performed, etc. Note that this process blank checked the subcontracting laboratory, but also the sampling process at the major hot-cell facility.
Standards	Analyze control standard(s)	•To confirm that the added reference material has not been compromised. If any characteristic of the standard has changed since it's certification (i.e. concentration, isotopic composition if a IDMS spike) the accuracy of the quantitative analysis will be compromised.	•Before addition of the standard to the samples •Note that some internal standards are present only qualitatively to monitor instrument stability or other experimental parameters. Certain attributes of these reference materials may not be as vulnerable as those employed for quantitative analysis
	Analyze spike composition	•To confirm that the spike has not been compromised. For example: evaporation causing concentration change, or contamination.	•Periodically, depends on the spike characteristics, how it is used, frequency of use. Typically defined in laboratory's quality assurance program.
	Addition of internal standard	•Added to the sample to track chemical yield, provide quantitative analysis, check instrument stability, etc. Not all analyses require internal standards as part of their quality control program but many do.	•Added prior to radiochemical processing.
Chemistry	Run a known sample that approximates the composition of the sample to be analyzed OR a sample of the standard/spike	•To confirm that the chemistry really works and there are no problems with any aspect of the methodology.	•Prior to sample analysis to identify and correct any chemistry problems prior to running samples or along with the sample to verify the chemistry worked as planned. This eliminates chemistry as a possible cause if analysis problems are identified downstream (i.e. during instrumental analysis).
	Run spike through the chemistry	•To confirm that a change in the spike composition has not affected the chemistry. •For example: growth of daughters (i.e. ^{212}Pb, ^{212}Bi) in ^{232}U spike used for alpha spectroscopy can cause problems in chemistry and in the alpha counting.	•Dictated by the growth rate of the daughters: typically every 6 to 12 months for the ^{232}U spike example.

*. Rule of thumb is the reagent should not contain more than 1/1000 of the species being measured.

Figure 14 provides an example flowchart of the quality control evolutions for analysis of uranium using isotope dilution mass spectrometry. This flowchart is a summary of the overall process and does not provide all details for the procedure and all quality control items. Typically all samples are performed in duplicate which is not indicated in this figure. The process blank is typically not diluted due to the very low concentrations of the constituents. It is also not unusual for the process blank to not be further subdivided to provide duplicate measurements.

Figure 14: Example of Quality Control Evolutions for Uranium Analysis



This section provided only a general summary of a quality control program as an educational tool. Actual quality control programs are much more involved. A successful quality control program verifies everything that happens to the sample: sample tracking, employed chemical reagents, air blowing into the hot-cell over the samples, labware cleanliness, complicated radiochemistry, added reference materials, instrumental analysis, calculations, and documentation.

IX. Trouble Shooting Experimental Problems

As illustrated by the preceding sections of this document, analysis of physics irradiation test program samples is a very complicated and challenging endeavour. However, talented subcontractors have the expertise and resources to take these challenges head on and provide high quality data. This section summarizes what a test sponsor should keep in mind when reviewing experimental results.

A. Remember "Assumptions" of Key Experimental Conditions

There are a number of conditions that must be maintained for successful quantitative radiochemical analysis. If the experimenter is capable, all of the conditions will be properly managed. Many of these conditions are not definitively proven and are "assumed" to be maintained. If any of these assumptions are untrue, then the experimental results can be in error.

The key assumptions are:

- the sample is completely dissolved,
- the analyte stays in solution until processed,
- there is complete mixing with the reference material and it remains in equilibrium with the analyte(s), and
- there are no chemical processes where isotopic fractionation occurs.

Physics irradiation test program samples are notorious for resisting both dissolution and, after dissolution, staying in solution. This characteristic can plague downstream analysis with problems that aren't related to the individual measurement techniques but occurred at an earlier stage directly affecting the parent solution.

B. Don't Forget Common Sense

One of the best tools in the determination of the "goodness" of experimental data is common sense. Physics always works: generally the more depleted the sample, the higher the fission products and transuranic species concentrations. This is physics, and if it isn't followed, there is either an experimental problem or someone forgot to take into account radioactive decay and/or production of a nuclide by more than one process. Appendix D provides greater detail on this topic and Reference 12 provides an excellent summary of fission product decay chains and the complicated parent/daughter decay/build-up schemes for the transuranics. Appendix A provides a good background on the essentials of experimental design and follow.

There are also numerous tools for tracking the quality of experimental data as it is being collected. For example, a burn-up correlation plot (plot ^{137}Cs per milligram of uranium as a function of the $^{236}U/^{235}U$ ratio) can be used to identify problems in the analysis. Significant dilution errors, swapped samples and other experimental problems can be identified early in the process and corrected.

C. Compare Experimental Results to "Expected" Values

Calculated values derived from physics models can be used for comparisons to experimental measurements. However, since the experimental measurements are performed to validate the models, these comparisons need to be treated accordingly. Despite this cautionary statement, these calculated "expected" values are very useful tools to use as a benchmark for the experimental method correctness. This is especially true when multiple measurements of the same samples by different laboratories cannot be performed.

Table 5 summarizes some common experimental problems and their effect on the final results. Additional details on trouble shooting experimental issues can be found in Appendix D.

Table 5: Summary of Some Common Experimental Problems

Occurrence	Possible Cause(s)	Effect on Experiment Results
Incomplete dissolution	•Chemistry inadequate, inadequate heating, not heated long enough	•Results lower than actual
Loss of sample	•Precipitation, co-precipitation, overheating of volatile chemical elements, adsorbing, polymerization, complexing	•Results lower than actual
Contamination	•Bad reagents, labware, contaminated air supply, sloppy processing	•Results higher than actual for some (but not always all) nuclides •Erratic results •Duplicate samples do not agree and are significantly outside the analytical error band
Dilution error	•Reported dilution larger than actual •Reported dilution smaller than actual	•Results higher than actual •Results lower than actual
Addition of internal standard (or spike) error	•Reported addition larger than actual •Reported addition smaller than actual •Spike solution more concentrated than documented •Spike solution less concentrated than documented •Wrong oxidation state for spike	•Results lower than actual •Results higher than actual •Results lower than actual •Results higher than actual •Results higher or lower than actual
Interfering species	•Incomplete separation, contamination, interfering species (mass or energy overlap)	•Results higher than actual for some (but not always all) nuclides
Mistaken identity	•Switching samples, mislabeling	•Random results

X. Lessons Learned and Best Practices

Appendix D provides a detailed account of best practices, lessons learned and experimental caveats for over three decades of radiochemical processing of physics irradiation test program samples and will not be reproduced here. However, remember the key causes for the failure of quantitative analysis when reviewing any physics irradiation test program results:

- incomplete dissolution,
- loss of analyte by co-precipitation or precipitation,
- incomplete separation,
- interfering species,
- contamination, and
- instrumental problems.

Carrier free radiochemical analysis of dilute solutions is very tricky when the required quantitative analysis of analytes is present at a level of 10^{10} atoms in a 10^{6} sample dilution. These dilutions cannot be avoided due to the sensitivity of the instrumental analysis and the need to reduce the radioactivity of the sample to a level safe enough to handle on the bench top.

It is unrealistic to assume no problems will occur - they will. It is also unrealistic to not check results while the experiments are in progress. Careful examination of the data as it is being produced can catch problems before they are propagated and at a point in time where they can be corrected. Examination of the experimental results for the first time months after the experiment's completion is not an effective way to monitor the quality of experimental results.

This document provided a number of definitions for radiochemistry terminology. Some terms were indicated to have multiple meanings depending on the discipline or even on a scientist's background and/or focus. For example, the definition of internal standard can have different meanings for different scientists. An internal standard may be an internal reference voltage for a scientist who primarily works with intrumentation. An internal standard to a radiochemist may refer to a precisely measured standard added to the sample to determine the efficiency of a chemical separation. An ICPMS scientist adds an internal standard to the solution prior to analysis to monitor instrumental instabilities. In addition to multiple meanings, a term may have a different name. For example, mass spectrometrists use the term "spike" for what is defined as an internal standard by other scientists. Always be clear that the terminology is understood by all participants; otherwise, information that is believed to be common to all, that is in fact not, may result in avoidable confusion.

XI. Conclusions

Accurate quantitative analysis of the wide variety of analytes of physics irradiation test program samples requires highly detailed expertise in a number of radiochemical analytical methods and meticulous execution. Veterans of these methods experience a 5-10% failure rate for concurrently run samples for "no good reason." It is unrealistic to assume that a subcontractor who has never run physics irradiation test program samples (or hasn't analyzed this type of irradiated samples in a few years) will be able to provide flawless analysis without some development samples to

process. A quality assurance program custom made for the samples and required measurements needs to be executed. The subcontracting laboratory also needs to provide additional data other than the experimental results to prove that some of the more likely errors have not occurred.

These physics irradiation test program samples are one of the most challenging samples for quantitative analysis. It is imperative to provide the subcontractor with as much detail as possible on the samples and provide all applicable information from the long history of sample processing. It is also prudent to supply “extra” samples for developmental purposes and to “practice” methods that have not been performed for a long time period. Whenever possible, additional test specimens should be supplied in case of a significant experimental problem. The overhead for the physics irradiation test programs is more costly than the actual processing of the samples. The incurred cost of providing a few additional samples is minimal and can be very beneficial.

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APPENDIX A

EXPERIMENTAL DESIGN AND FOLLOW

1. Introduction

This document provides the necessary background to construct and execute new physics irradiation test programs. Information specific to irradiated test specimens, lessons learned, noted ideas for improvements and documentation of procedures that "didn't" work in addition to what worked have been included in the experimental documentation. This appendix provides further guidance in developing and following irradiated test physics exams to provide the best possible data. Please note that the information provided is valid at the time of its writing and the validity may change with time as procedures and/or policies change.

This appendix is written in a casual style and assumes that the reader will be a test sponsor. Frequently the test sponsor is different from the end user of the data. When they are the same person, the task is a bit easier. If you are not both the test sponsor and the end user, make certain that you have excellent communications with the end user and understand not only what the end user wants measured, but why. There is nothing incredibly profound in this appendix. Most of the topics deal with exercising good common sense.

Please note that the material in this appendix is my opinion formulated over a decade of experience and is not all inclusive. I present this information here since parts have been valuable to new entry test sponsors for physics irradiation test programs. Also be aware that many things can change over time and some of the particulars between the writing of this appendix and the reading of this appendix may have changed significantly.

2. Background

Physics irradiation test programs are one of the most difficult categories of experiments to execute. The samples are highly radioactive so that shipping, processing and waste issues are paramount to the processing of these samples. The samples will need to be dissolved and processed, which adds the complexities of having highly radioactive samples that are now dissolved in potentially hazardous chemicals. And if that isn't enough to deal with, some samples (and associated data) require special handling for information protection purposes. Added to these challenges are regulations that are in constant flux: shipping requirements, handling requirements of highly radioactive samples, chemical and radioactive waste disposal, etc. Analytical procedures are also constantly changing. The majority of the changes are positive in that the analytical procedures improve with research and improvements in instrumentation and new techniques. However, care must be made in changing the procedures to ensure that they provide successful analyses. Other changes result in significant challenges. For example, a particular reagent is no longer available or the handling restrictions make it administratively difficult to use the reagent thus completely changing the analysis procedure. This has happened frequently during the history of radiochemical analysis - the best method of separation uses a reagent that regulations have made "too hot to handle," or the liability of manufacturing the reagent has forced the manufacturer to stop production. Unfortunately, the substitute procedure for a few analyses is inferior to the original procedure, but these luckily are so far quite rare. As environmental

issues continue to put more restrictions on chemical manufacturers and laboratory facilities, the situation could become more commonplace in the future. Hopefully future breakthroughs in technology may provide alternatives to the separation of the individual components.

In addition to changes in methods and equipment for analysis, these exams are expensive to perform and there are fewer and fewer facilities that will perform these measurements. There is also the fact that true radiochemists are getting harder and harder to find since the universities have cut back or eliminated this area of study.

3. Know Your Experimental Requirements

So let us start at the beginning: what is being measured, how well does it need to be measured, and in what matrix do the analytes [a] exist? The more you know about these three basic requirements, the better you will be able to design and successfully execute the experiment to provide meaningful data.

One of the unpublicized responsibilities of the test sponsor is to ensure that the data you will collect "makes sense". The following questions may appear somewhat "silly" but I have seen these errors made repeatedly by very intelligent test requestors.

- Are you measuring a species that is gaseous and that will be partially lost in the sampling process?
- Are you measuring a species that is radioactive and is now mostly decayed away due to the time between the end of the irradiation and the subsequent analysis?
- Was the sample's pre-irradiation composition characterized well enough to provide meaningful data for the end use study?

If you are the test sponsor and not the end user, do not assume that your end user has considered these "obvious" issues. It is YOUR job to address these types of questions.

4. Know Your Starting Material

The collected data will most likely be compared to the starting material. For example, to determine the burn-up of the fissile isotope, the sample's fissile isotope quantity measured at end of the irradiation is subtracted from the sample's fissile isotope quantity prior to irradiation. Thus the total uncertainty in the final quantity of interest will not only be the experimental uncertainty, but will include the uncertainty on the pre-irradiated fissile isotope content. The more information you have on the starting material the better. This includes pre-irradiation data such as elemental quantities, isotopic composition, and spatial distribution in the sample.

5. Know Your Samples

It is important to have intimate knowledge of your samples. What is the composition of the sample: major constituents, trace elements, etc.? What is the expected range of the analytes to be measured? The chemists will want to know what is to be measured, approximately how much is present, what else is in the sample and what are the accuracy requirements. It is imperative to give them approximate values of the major constituents, any known trace elements and the expected range of the analytes to be measured. This is NOT cheating. The chemists need this information to efficiently design their separations, determine required dilutions and determine required spike amounts for procedures that

[a] measured species (elements or isotopes) of interest

employ them. It is sufficient to provide the expected range as order(s) of magnitude (e.g.: an expected range for ^{235}U of 0.1 to 0.001 grams/test specimen).

6. Know Data's Major End Uses

How are the data going to be used? This is a very important question and, at an extreme, could result in not performing the measurement. For example, if the end user wants quantitative measurements of Element X from the irradiated test specimen, then you need to ask what they are going to do with the data. They tell you that they want to know the amount of Element X resulting from uranium fission. Since you "know-your-sample", you know that the irradiated sample contained Element X prior to irradiation. So what do you do? You notify the end user of this fact and you also cheerfully inform them that you "know-your-starting-material" and that you have pre-irradiation measurements for all isotopes of Element X and they are known to an accuracy of X%. The end user will probably know expected values for the fission product of Element X and has already specified the required accuracy of the end of irradiation determination. With these pieces of information you and the end user can determine if it makes sense to do the determination. If the pre-irradiation content is only known to, for example, 50%; it is present in quantities comparable to what would be produced by fission, and the required accuracy of the measurement is 5%, then the total uncertainty in the measurement may result in the final data not being very useful. Note that the end user should know the approximate quantities of their species of interest. If they don't, they haven't done their homework and/or thought hard enough about the measurements and what they are going to do with them. I strongly recommend that you push them to do this work up front if at all possible.

There is another issue that frequently gets ignored. When determining that a measurement is accurate enough to satisfy an end user, one must consider the total experimental error. For example, the end user runs a calculation using two different cross section libraries which provides two different results that vary by 3% and wants the experiment to tell them which cross section library provides the "correct" answer. Let's assume your measurement uncertainty is only 0.02%, but the uncertainty in the pre-irradiated sample composition is 3.5%, and the sampling error is 8%. This total experimental uncertainty is calculated to be about 8.7%. With an experimental uncertainty of almost 9%, the experiment does not have the required "sensitivity" to make a 3% distinction. This is the case when both calculational results fall within the errors of the measured results. Now, it is an entirely different issue if BOTH results fall outside of the range of the measured values and their experimental errors. Thus, you need to know the type of measurement, how well it has been measured in the past and how did it agree with calculations. For previously analyzed analytes in new materials, or never before measured analytes, it is appropriate to perform the experiment (requesting best effort by the subcontractor) to provide base line information.

7. Everything is Relative – or Absolute

It is important to know what is measured and how it is reported. Most experimental results performed for physic irradiations test programs are quantitative, which means that the analyte is reported as an absolute quantity (e.g.: atoms of ^{137}Cs per test specimen). But some measurements are qualitative (also referred to as relative) such as isotopic weight percents, atom ratios, and the like. Quantitative measurements are more difficult (thus more expensive) to execute because the chemistry needs to be performed in a way to trace absolute quantities, and usually well characterized standards (sometimes employed as spikes or tracers) need to be employed.

Note that absolute measurements can be combined with relative measurements to provide quantitative results. For example, quantitative uranium isotopes can be calculated using the isotopic weight percents (relative results) and the total grams of uranium in the sample (absolute measurement). It is important to know what is being measured and reported to ensure that the end user obtains the necessary data.

8. Beware of Folklore

There are many statements that are used out of context, or simply not true, but have been passed on as tribal knowledge from one individual to the next. It is important to track down folklore to determine if it is true, taken out of context, or unsupported by the available information[b]. Do not take all information at face value and always maintain a questioning attitude.

There is also a lack of documentation on experimental execution and how exactly things were done in the past. In following physics irradiations test programs I came across many gaps in documentation and it was very difficult to find adequate documentation for some procedures and/or equipment. People relied on the "tribal knowledge" passed on from engineer to engineer at the facility. Some of it was correct and verifiable, and other information could not be verified and an educated "guess" had to be made. This should be avoided in the experimental process.

9. No One is an Expert on Everything

As you can surmise by reading this document, these experiments involved many areas of expertise. No one person can know it all. You need to identify the experts with which you need to make contact early on. Sometimes as early as the stage when you are determining if the measurement can be made in the required substrate, and certainly by the time you sit down to write the technical specifications. Have them review their respective sections of the technical specifications. Remember that you cannot be an expert on everything, but your function as program manager is that all the right people are involved at the proper level and that all the components are integrated with no "holes" in the procedures and/or execution.

10. The Art of Writing Technical Specifications

Writing technical specifications are difficult for any experiment. The technical specifications need to be very detailed so the test sponsor will get exactly the information they want in the required timetable, but at the same time be flexible to allow the performer to execute the experiment in the most efficient way to provide the best possible data. This is the ultimate challenge - to write a flexible, yet detailed, technical specification. An effective method is to first start with a detailed table of what is to be measured, how well it needs to be measured, and then really understand the end use of the data. Be careful of picking up and altering an old technical specification. Oftentimes equipment and techniques have changed or are not applicable to the end goals of the new experimental program. Old technical specifications are a good starting point to use as an example and a launching point to investigate what has changed and what is the same. Also note that different end users have different goals and the basic function of the technical specification is to supply the correct measurements with the required accuracy. A way to provide enough details for the subcontractor to construct their methods with the best possible end result is to provide one detailed example for one of the analytes. A smart subcontractor will be able to extrapolate the amount of detail to other procedures. Always request that

[b] polite phrase for just plain un-true

the subcontractor provides a draft of their work plan for your review and sign off. This gives you the opportunity to provide more information and/or comments to their technical work.

It is imperative to define the level of quality assurance and type of quality assurance data that is needed. This requires specialized knowledge. If you are not a chemist, go seek the help of one to determine what is needed.

Don't forget to specify the required documentation. Documentation is just as important as the data. If the measured data match calculated values exactly there is usually no grilling of the experimentalists. However, if there is a disagreement, the experiment will receive a high level of attention and all involved with the experiments are interrogated. If you don't have the proper documentation to address the questions, you run the risk of the data being put on a shelf and people remarking – "yes, generally the data agreed with the model but there were some data that just didn't-look-right." If there is a question between the calculated and the experimental values, the actions to resolve the disagreement usually fall on the experimentalist. Is this fair? The answer depends on whether or not you are an experimentalist. This unfortunate fate of the experiment data was avoided in these experiments by requesting additional data. So when someone said "well, that plutonium value is too high compared to predictions so the samples must have been contaminated in the hot-cells," we could pull out the plutonium data for the process blank and reagent blanks run with the samples through the hot cells and show that there was no gross plutonium contamination in the hot cell. Note that this does not rule out a possible "sporadic" contamination of an individual sample, however, it does rule out contamination of the entire batch of samples, which was the accusation.

Always provide draft technical specifications to the technical experts you have consulted and the individuals actually performing the experiment to provide feedback. Don't rely only on management as they are often not the technical experts in all of the required areas. Also, if there are technicians involved, make certain that they review the draft as well. They are typically the best sources for information since they are the ones performing key parts of the exams. The quality of your experimental results often rests in their capable hands.

11. Know Your Subcontractor

The quality of the experiment measurements is directly correlated to the ability of the subcontractor. It is imperative that not only does the subcontractor have the required facilities and instrumentation, but that the scientists know what they are doing. Classical radiochemistry is becoming a lost art form with many of the new radiochemists not possessing the depth of knowledge of the "old-timers". The advantage of many of the radiochemists that worked in the field since the 1950s, 1960s, and 1970s is that they were "classic" separation radiochemists with very solid wet chemistry skills and also very knowledgeable in the area of nuclear physics. Many radiochemists also had physics degrees.

Do not assume that just because the subcontractor provided good results in the past that they will continue to do so. Many laboratories are doing away with certain capabilities having high overhead. Loss of a major project can also impact capabilities and quality assurance. Key retirements without good cross training can seriously affect capabilities. Many techniques require complex instruments that need extensive upkeep and replacement. Keep in contact with the subcontracting laboratory and track the capabilities and personnel key to your analyses.

12. Follow, Follow, Follow

I absolutely can't stress this fact too much. You can't just send the technical specification off and assume that your job is done: that is where the work really starts. Know the people doing the work. Visit the site, talk with the scientists and technicians, discuss the quirks of the samples, share the problems we've experienced and keep your eyes and ears open. Demonstration that you really care about the results will get you better results. The test performers will be more likely to contact you if something "just doesn't look right".

Now remember to be tactful in how you follow the work: don't hover like an auditor looking for a problem. This will not foster a cooperative relationship. It is very effective to continuously ask questions from a learning perspective. This is a way to become more knowledgeable and sometimes questions trigger a realization on the part of the chemist.

Whenever possible, examine the data as soon as they become available. We requested faxed preliminary data to review the results. Oftentimes problems can be identified and corrected immediately. Remember to do "reality" checks on the data. For example, the quantities of fission products[c] should directly correlate with uranium depletion. If it doesn't, then there is a problem somewhere. "Back-of-the-envelope" calculations are very useful to determine if the results "make sense". Fission products should be produced in their relative fission yields that are found on the chart of the nuclides. It is also extremely valuable to have the calculations that the experimental results will be compared to. Yes, we are usually performing the experiments to check the validity of the calculated values using various modeling programs. So isn't it a bit incestuous to use the calculations to "verify" the experimental results? Bottom line is that history has showed us that these modeling programs do a pretty good job of "predicting" results. It is another tool: compare experimental to calculational results (knowing the comparisons for what they are). When you see big discrepancies, talk to the end user. Oftentimes they know of "deficiencies" in their models and can shed light on the differences; or not.

13. Communication, Communication, Communication

Another issue that can't be stressed enough is communication. Assume nothing. It is better to tell someone a fact twice or something they already know than to say nothing and potentially have an essential fact realized at too late a date. Many issues were avoided by having open communication between the test sponsor, end user, all related central test facility personnel (including purchasing and shipping), and the subcontractor (chemists and security personnel). Never forget to include the actual test performers. Don't rely on management to provide the required information to the people on the deck plates: you need to maintain personal involvement with all personnel. Make a list of people early on in the program tracking all involved personnel…even the person you need to call to send a classified fax.

Keep in mind that some scientific terms can have multiple meanings to different scientists and for different applications. Other terms may be referenced using different names. It is imperative that all involved parties share a common definition for these types of terms. Make certain that everyone is using the same definition or there will be a disconnect where everyone thought they knew what they were talking about – but didn't!

A note on "need-to-know" information: remember, these people are smart - that is why we hired them. When they see a usual isotope of a particular element in the test specimen that shouldn't logically be

[c] Don't forget to correct for decay if it is an unstable nuclide. Also, some nuclides build up from the decay of other nuclides.

there they are going to notice. If they are not informed about the fact that they may see this particular isotope, they will first believe they have a problem with their chemistry. The result will be that they will spend resources investigating something that does not contribute to the measurement. They will eventually ask us: “What is the deal with the presence of isotope X for element Y in this type of sample?”; possibly in an unsecured form of communication. So they have a need to be forewarned of certain “need-to-know” information. Past practice of telling the analyst nothing about our samples has been detrimental to our experiments. So find the balance point - if the protected information affects the analysis, that information needs to be forwarded in the appropriate manner and ensure that the information is properly protected.

14. Know Your Role

You are not the person facilitating the contract with the subcontractor. The contract is facilitated by others (usually in procurement) and often administered by another facility. Follow the contract manager’s protocol for interactions with the subcontractor. Remember to NEVER discuss money or contract issues with the subcontractor: you are technical support ONLY. It goes without saying to always conduct relations with the subcontractor in a strictly professional manner.

Also be very mindful of what the subcontractor considers to be proprietary and always appropriately protect that information. A good practice to follow is if there is any doubt whether information is proprietary, assume that it is.

15. Summary

Probably the most important aspects in designing an experimental program is painstaking attention to detail and thinking through the entire process from test specimen fabrication prior to irradiation to the application of the final data. The most important aspects in following an irradiation test program is communication (with everyone), and careful attention to all experimental details while keeping an eye on the “big picture”. Remember to not get buried in the details and miss the forest because of the trees. The “big picture” needs to make sense. Physical laws apply and a little common sense goes a long way in this type of project. Also remember that due to the long life span of some of these experiments (e.g. may take three years or longer from start to finish), expect things to change mid-stream (i.e. shipping regulations, waste disposal protocols, etc.). Good luck!

APPENDIX B

COMMON CALCULATIONS

1. Introduction

This appendix provides key calculations used to calculate the data presented in typical physics irradiation test program reports. It is not inclusive of all employed calculations. Many minor calculations were used, such as dilution calculations and conversion from grams to atoms, and these are not detailed in this appendix.

2. Conversion Calculations

A number of conversions were performed in the calculations and are provided here for the reader's convenience. Remember whenever making a unit conversion to explicitly list the units for each value and make certain that they properly cancel out to provide the answer in the desired units. Since experimental data are provided in a myriad of different formats (i.e. micrograms, milligrams, grams; counts per minute, counts per second), the user must ensure that the correct conversion calculation is used.

a. Activity to grams

The units for final data are provided as grams of the analyte per test specimen. Most subcontractors will provide results for radioactivity in activity units, not as grams. The following paragraphs explain how to convert measured activity to grams of analyte.

The measured activity is defined as $A = N \lambda$ and each term of this equation is defined with its units in Table B-1.

Table B-1: Activity Equation Components

Attribute	Symbol/Equation
Measured activity	A is commonly reported as counts (disintegrations) per second
Number of atoms of radioactive nuclide	$N = \frac{\text{grams of radioactive nuclide in the sample} * 6.02252 \times 10^{23} \text{ atoms/mole}^{a}}{\text{atomic weight (g/mole)}}$
Decay constant for radioactive species:	$\lambda = \ln 2 / \text{half life}^{b}$ of radioactive nuclide (commonly in seconds)

Note that the decay constant and activity need to be in the same units of time. It is a common error to mix time units. Using the formula for the measured activity, and the equations provided in Table B-1 activity of a sample can be converted to grams using the following formula:

$$g = \frac{A \text{ (atoms/sec)} * \text{Atomic Weight (grams/mole)} * t_{1/2} \text{ (sec)}}{6.02252 \times 10^{23} \text{ (atoms/mole)} * \ln 2} \qquad \text{(Equation 1)}$$

[a] Avogadro's number.
[b] half life is $t_{1/2}$

Note how the units on the right cancel out to provide grams. Very often the subcontractor will provide results per gram of sample. In that case the user needs to multiply the result by the sample weight to provide the grams of the nuclide of interest for the entire sample. Solve Equation (1) for the activity term to convert grams to activity.

b. Curies to grams

Sometimes the subcontractor will provide activity measurements in curies (Ci). This unit is common for radiological control purposes and for shipping applications, since many regulatory agencies employ curies as the unit of choice. Curie is a unit for the disintegration rate defined as 3.7×10^{10} disintegrations/second. The unit is historically derived as the quantity of radon in equilibrium with one gram of radium. This unit is being replaced by the Standard International (SI) equivalent of Becquerel[c]. Use the following Equation to convert curies to grams:

$$g = \frac{(A\ (Ci) * 3.7 \times 10^{10}\ atoms/Ci\text{-}sec) * Atomic\ Weight\ (grams/mole) * t_{1/2}\ (sec)}{6.02252 \times 10^{23}\ (atoms/mole) * \ln 2} \quad \text{(Equation 2)}$$

Note how the units on the right cancel out to provide grams. Very often the subcontractor will provide results per gram of sample. In that case, the user needs to multiply the results by the sample weight to provide the grams of the nuclide of interest for the entire sample. Again, take care in having the appropriate units for a correct conversion. Solve Equation (2) for the activity term to convert grams to activity.

3. Propagation of Errors

The majority of the data provided in physics irradiation test program reports are a result of a series of measurements. The total experimental error needs to be calculated using the individual errors for each measurement. The following provides the specific formulas commonly used for the propagation of errors for a series of measurements[d]. Please note that some of the minor terms in some of the mathematical formula are neglected due to their relatively small[e] contribution and that the formulae being provided for error propagation is predicated on the assumption that errors are uncorrelated and statistically independent.

a. Addition and subtraction

In addition and subtraction, the total uncertainty is estimated by calculating the square root of the sum of the variance for each measurement. The variance is an estimate of the individual measurement uncertainty and is typically calculated by squaring the standard deviation of the measurement.

For example, the perimeter P of a rectangle is defined as twice the sum of the length plus the width ($P = 2L + 2W$). If the length and width were each measured twice to evaluate the perimeter, then the uncertainty in P would be defined as:

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[c] 1 Bq = 2.703×10^{-11} Ci (1 disintegration/second).
[d] A complete treatise on this topic can be found in Philip R. Bevington, "Data Reduction and Error Analysis for the Physical Sciences,"McGraw-Hill, Inc. (1969).
[e] Small is defined as a contribution less than the least significant figure of the measurement.

$$\sigma_P \simeq \text{square root}(\sigma_{L1}^2 + \sigma_{W1}^2 + \sigma_{L2}^2 + \sigma_{W2}^2) \quad \text{(Equation 3)}$$

where: σ_{L1}^2 is the variance for measurement of the first length,
σ_{W1}^2 is the variance for measurement of the first width,
σ_{L2}^2 is the variance for measurement of the second length, and
σ_{W2}^2 is the variance for measurement of the second width.

If the uncertainties are given as: σ_L = 2 mm and σ_W = 1 mm, then the uncertainty would be approximately 3.2 mm.

b. Multiplication and division

In multiplication and division, the total uncertainty is estimated calculating the square root of the sum of the variance (typically calculated by squaring the standard deviation) divided by the mean for each measurement. This calculated square root is then multiplied by the measurement's mean.

For example, the area of a triangle (A) is equal to half the product of the base (b) multiplied by the height (h): ($A = ½b * h$) and it's uncertainty for the area (σ_A) is estimated using the following equation:

$$\sigma_A \simeq A * [\text{square root}(\sigma_b^2/b^2 + \sigma_h^2/h^2)] \quad \text{(Equation 4)}$$

where: b is the base measurement,
σ_b^2 is the variance for measurement of the base measurement,
h is the height measurement, and
σ_h^2 is the variance for measurement of height measurement.

If the base measurement is 5 cm and the height is 10 cm, then Equation 4 becomes $\sigma_A \simeq 25 * [\text{square root}(\sigma_b^2/25 + \sigma_h^2/100)]$. If the uncertainties were given by σ_h^2 = 1 mm and σ_b^2 = 3 mm, the calculated uncertainty in the area would be 9 mm^2.

4. Decay Corrections

The majority of the species were not decay corrected. When data were corrected to a common date, the decay calculation was performed as illustrated in Table B-2.

Table B-2: Decay Correction Calculation Components

Attribute	Symbol/Equation
Measured activity at Time "t":	A
Activity at t = 0:	A_o
Decay constant for radioactive species:	λ = ln2/(half life of radioactive species)
Radioactive decay equation:	$A = A_o e^{-\lambda t}$
Correction factor to correct measured activity (A) at time of the measurement (t) to the activity at t = 0:	$1/e^{-\lambda t}$

The end of the irradiation is commonly defined as the time equal to zero and the analysis date is time "t". Make certain that the time units are the same for all of the equation's time related factors or erroneous correction will be used.

The end user needs to note that a simple decay correction cannot be used for some of the measured nuclides where the nuclide is decaying, and is also being formed by the decay of another species. In these cases it is very difficult to correct the measured data. The easiest solution is to extend the model calculation at zero power to the analysis date. However, this only works if the model includes all of the relevant decay chains.

5. Isotope Dilution Mass Spectrometry Calculations

There are a number of calculations performed for isotope dilution mass spectrometry. It can be tedious to reproduce the subcontractor's calculations because there are a number of corrections that must be made (i.e. spike isotopic abundances, mass fractionation, blanks, and multiple detector biases), the corrections can be applied in different places in the calculation (i.e. bias correct atom ratios or bias correct the atom percents), and different laboratories use different units (i.e. atom ratios or weight ratios, atom percents or weight percents). So although the calculations are quite simple, it is easy to make errors due to different units and correction factors. The executed calculations can be found in the appendices containing the raw data and/or in the references provided in each chapter of reports detailing each individual experiment. The primary calculations are provided in this section: mass fractionation corrections, isotopic ratio to atom percent conversions, and isotope dilution calculations.

a. Mass fractionation corrections

Mass fractionation occurs when atoms are ejected in the source of a mass spectrometer. Two phenomena occur in this process: the atom is ejected from the filament and then ionized. Ionization properties are dependent on the chemical element, loading method[f], and the physical characteristics of the filament. Thus, the mass fractionation correction is a function of the chemical element being analyzed. Mass fractionation occurs because lighter isotopes are ejected easier than heavy isotopes for a chemical element. The majority of thermal ionization mass spectrometer software will report atom ratios. Thus, the measured atom ratio of (for example) $^{235}U/^{238}U$ will be larger than it is in the sample because ^{235}U is more easily atomized than ^{238}U. The mass fractionation correction factor[g] is typically reported as the bias fraction per atomic mass unit (amu) since mass fractionation is linear over the mass range for the isotopes. This mass fractionation correction factor is both instrument and sample dependent and must be calculated based on the measurement of at least one ratio of a certified material. Also note that this mass fractionation correction factor does not necessarily remain constant with time and typically the factor is measured each day as a routine checkout of the equipment. The calculation of this factor and its use can be more easily illustrated using the following example.

One subcontractor calculated their bias based on the measurement of the $^{235}U/^{238}U$ ratio of a certified material. They used one of their in-house controls which is NBS U-750 spiked with high purity ^{233}U and has the composition provided in Table B-3.

[f] The chemical form (i.e. nitrate), the solvent (nitric acid) and any other chemical substance added to the loading solution to aid in the ionization process.
[g] Also referred to as the mass fractionation bias factor which is sometimes confusingly shortened to the "bias factor".

Table B-3 Composition of Certified Material Used in Uranium Bias Calculation

Isotope	Atom Percent
233	10.8587
234	0.5280
235	67.1741
236	0.2228
238	21.2165

The mass fractionation correction bias was calculated as percent per mass unit:

$$\textbf{\textit{Bias fraction}} = 100 * \{[(\text{observed } {}^{235}U/{}^{238}U)/ (\text{certified } {}^{235}U/{}^{238}U)] - 1\}$$

The correction is applied to the measured data which is in the form of normalized atom percents (calculated from atom ratios):

Corrected atom % = uncorrected atom% * [1-(bias fraction) * Δmass]

where the bias fraction is the bias percent/100 and Δmass is the difference between mass 238 and the mass of interest. The corrected atom percent values are then re-normalized to 100%.

Use common sense when checking results. As explained above, ^{235}U is more readily atomized than ^{238}U. Corrected $^{235}U/^{238}U$ ratios (lighter mass in numerator) should be smaller than the uncorrected ratios. When the heavier mass appears in the numerator, the corrected ratio should be larger than the uncorrected ratio.

b. Isotopic ratio to atom percent conversion

Most thermal ionization mass spectrometer software will report data as isotopic atom ratios of the element being analyzed. The following equations illustrate how raw uranium isotope ratios are converted to atom percents for each uranium isotope.

The calculations are complete provided that the following assumptions are true:

- if a multiple collector detection system was used, all detector efficiencies are exactly the same,
- there are no isobaric interferences (i.e. ^{238}Pu at mass 238), and
- the only uranium isotopes that are in the unspiked sample are ^{234}U, ^{235}U, ^{236}U and ^{238}U.

If the above assumptions are not true, then the appropriate corrections need to be applied.

The calculation is as follows:

Knowns: **A** = $^{234}U/^{233}U$; **B** = $^{235}U/^{233}U$; **C** = $^{236}U/^{233}U$; **D** = $^{238}U/^{233}U$

Calculate R_i (raw atom percent[h] of isotope i)

$$\mathbf{R_{234}} = A * R_{233} \quad \text{(Equation 5)}$$

$$\mathbf{R_{235}} = B * R_{233} \quad \text{(Equation 6)}$$

$$\mathbf{R_{236}} = C * R_{233} \quad \text{(Equation 7)}$$

$$\mathbf{R_{238}} = D * R_{233} \quad \text{(Equation 8)}$$

$$R_{233} + R_{234} + R_{235} + R_{236} + R_{238} = 100 \quad \text{(Equation 9)}$$

Substitute Equations (5) through (8) into Equation (9):

$$R_{233} + A * R_{233} + B * R_{233} + C * R_{233} + D * R_{233} = 100 \quad \text{(Equation 10)}$$

Rearrange:

$$R_{233} * [1 + A + B + C + D] = 100 \quad \text{(Equation 11)}$$

Solve for R_{233}:

$$\mathbf{R_{233}} = 100/[1 + A + B + C + D] \quad \text{(Equation 12)}$$

Substitute back into Equations (5) through (9) to calculate other R_i values.

These atom percents are then used to calculate uranium isotope concentrations as described in the next section.

c. Isotope dilution calculation, type I

Details on isotope dilution mass spectrometry technique can be found in Section VII of this report. For a typical isotope dilution calculation, two mass spectrometric measurements are made. An aliquot of the sample solution is run without any added spike solution. This is referred to as the "unspiked" solution. From this measurement, the isotopic abundance for each isotope is calculated. The other mass spectrometric measurement is performed for a sample aliquot to which a precisely known quantity of spike has been added. This is referred to as the "spiked" solution and the measured ratios of the unknown to the spike isotope allow the calculation of the quantity of unknown in the sample solution.

If the major spike isotope is not present in the unspiked solution, then a simplified isotope dilution method is employed and only a spiked solution is measured. This section will provide an example of how uranium isotope concentrations are calculated from the experimental data using this simplified method. This example also includes corrections for mass fractionation and the spike contribution[i] to uranium isotopes in the solution. In cases were the spike isotope is present in both the spiked and unspiked sample, additional calculations must be performed and will be summarized after this sample calculation.

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[h] Raw atom percent typically refers to the atom percentage calculated from the raw atom ratios provided by the instrumental software. However, with multiple collector instruments, often the raw atom ratio has been corrected for the differences in the detector efficiencies. This is not standardized, and the end user needs to inquire what corrections (if any) are made by the software. Raw atom ratios from ICPP/INTEC are already included the detector efficiency corrections. If the detector efficiency corrections are not made, then these atom percents need to be corrected for the detector efficiencies. For the purposes of this example all detector efficiencies were exactly the same.

[i] The spike is not 100.00000% ^{233}U. It contains small amounts of ^{234}U, ^{235}U, and ^{238}U.

Table B-4 provides the data for the sample calculation. The calculation is broken into six parts and is detailed in the six steps immediately following the data table.

Table B-4: Data Used for Uranium Isotope Dilution Sample Calculation

Attribute	Value	Units and/or symbol
Spike solution weight	0.99603	grams
Spike concentration	1.910727×10^{-4}	grams ^{233}U per gram of spike solution
Sample solution weight	1.4126	grams
Uranium concentration of sample	Being calculated	grams of uranium/gram of sample solution
Spike composition ratios	1.811368×10^{-4}	$^{234}U/^{233}U$
	1.10083×10^{-5}	$^{235}U/^{233}U$
	0	$^{236}U/^{233}U$
	5.634254×10^{-4}	$^{238}U/^{233}U$
Atomic weights	233.039628	^{233}U (grams per mole)
	234.040945	^{234}U (grams per mole)
	235.043922	^{235}U (grams per mole)
	236.045561	^{236}U (grams per mole)
	238.050785	^{238}U (grams per mole)
Bias (mass fractionation correction)	0.0615	% per amu
Raw mass spectrometer ratio data:		
$^{234}U/^{233}U$	0.0091201	R1 (uncorrected atom ratio)
$^{235}U/^{233}U$	0.8379974	R2 (uncorrected atom ratio)
$^{236}U/^{233}U$	0.0037405	R3 (uncorrected atom ratio)
$^{238}U/^{233}U$	0.3427949	R4 (uncorrected atom ratio)

Step 1. Calculate raw atom percent from mass spectrometer ratios:

$\%^{233}U = 100/(R1+R2+R3+R4+1) = 45.58606$

$\%^{234}U = R1 * \%^{233}U = 0.41575$

$\%^{235}U = R2 * \%^{233}U = 38.20100$

$\%^{236}U = R3 * \%^{233}U = 0.17051$

$\%^{238}U = R4 * \%^{233}U = 15.62667$

Step 2. Bias correction for raw atom percents calculated in Step 1:

Corrected atom % = raw atom% * [1-{bias fraction * (238-mass number of isotope)}]
(where bias fraction = (bias as percent)/100):

At%^{233}U	At%^{234}U	At%^{235}U	At%^{236}U	At%^{238}U	Sum[j]
45.44588	0.41473	38.13052	0.17030	15.62667	99.78810

Re-normalize:

45.54239	0.41561	38.21149	0.17067	15.65985

Step 3. Remove spike contributions from bias-corrected atom percent calculated in Step 2:

Correction = {bias-corrected atom percent for ^{233}U (*calculated in Step 2*)} *
{isotope ratio to ^{233}U of spike composition ratio[k] for each isotope}

At%^{233}U	At%^{234}U	At%^{235}U	At%^{236}U	At%^{238}U
45.54239	0.0082494	0.0005013443	0	0.0256597

Subtract the correction from bias-corrected atom percent result calculated in Step 2:

At%^{233}U	At%^{234}U	At%^{235}U	At%^{236}U	At%^{238}U	Sum[l]
0	0.40736	38.21099	0.17067	15.63419	54.42321

Re-normalize:

0	0.74850	70.21083	0.31360	28.72706

Step 4. Convert spike-corrected atom percent calculated in Step 3 to weight percent:

Atom % * atomic weight; then renormalize:

Wt ^{233}U	Wt ^{234}U	Wt ^{235}U	Wt ^{236}U	Wt ^{238}U	Sum[m]
0	175.18	16502.63	74.0239	6838.499	23590.33

Re-normalize:

Wt%^{233}U	Wt%^{234}U	Wt%^{235}U	Wt%^{236}U	Wt%^{238}U
0	0.74259	69.95506	0.31379	28.98857

Step 5. Convert from bias-corrected atom percent calculated in Step 2 to bias-corrected weight percent[n]:

Atom % * atomic weight; then renormalize:

Wt%^{233}U	Wt%^{234}U	Wt%^{235}U	Wt%^{236}U	Wt%^{238}U	Sum[o]
10613.182	97.270	8981.378	40.286	3727.840	23459.96

Re-normalize:

45.23956	0.41462	38.28386	0.17172	15.89022

[j] For renormalization to 100%.
[k] From Table B-4.
[l] For renormalization to 100%.
[m] For renormalization to 100%.
[n] The only need for this step is to get the ^{233}U for use in the IDMS calculation.
[o] For renormalization to 100%.

Step 6. Isotope dilution calculation for grams of uranium per gram of sample solution[p]:

Spike weight (g ^{233}U) = Spike solution weight * concentration of ^{233}U in spike solution
= 1.9031×10^{-4}

Concentration (g U/g of sample solution)
= [(100/W)-1] * (calculated spike weight/sample solution weight)
where W = bias-corrected Wt% of the spike isotope (^{233}U) from Step 5
= 1.6308×10^{-4} g U/g of sample solution

The total weight of uranium in the sample solution can be calculated by multiplying this concentration by the total weight of the sample solution:

grams of uranium of sample solution = (1.6308×10^{-4} g U/g sample) * 1.4126 g sample
= 2.3037×10^{-4} gram of uranium

Step 7. Calculate the weight for each uranium isotope in the solution:

The weight of each uranium isotope in the sample is calculated by multiplying the total weight of uranium by each isotopic abundance calculated in step 4:

grams of ^{234}U = (0.74259/100) * 2.3037×10^{-4} = 1.7107×10^{-6}

grams of ^{235}U = (69.95506/100) * 2.3037×10^{-4} = 1.6116×10^{-4}

grams of ^{236}U = (0.31379/100) * 2.3037×10^{-4} = 7.2288×10^{-7}

grams of ^{238}U = (28.98857/100) * 2.3037×10^{-4} = 6.6781×10^{-5}

If a reagent and/or process blank is performed, the weight for each uranium isotope in the blank is determined using the above method through Step 7. The blank correction for each uranium isotope is then subtracted from the corresponding isotope calculated for the sample.

This is only one method of performing this calculation. One alternate calculation can be found in Appendix D.

d. Isotope dilution calculation, type II

The preceding example is a simplified isotope dilution calculation and can be used only if the sample has no significant[q] ^{233}U. This section provides the concept and equations in the case when the sample contains multiple isotopes of the major spike isotopes. For simplicity, the equations will illustrate an isotope dilution calculation where the sample and the spike have two isotopes. The classic textbook example of boron as a two isotope system will be employed. The equations can be expanded for use with elements having more than two isotopes. No other corrections (such as mass fractionation basis) will be included in this example set of equations.

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[p] Note that oftentimes the subcontractor will provide the results as concentrations (grams of uranium per gram of solution). In this case, the total weight of uranium in the test specimen can be calculated by multiplying the concentration by the total weight of the parent solution.

[q] All samples will have trace amounts of ^{233}U, but are usually statistically insignificant if corrected for. For example, ^{233}U was present in these samples in the amount of a few parts in a hundred thousand. One unspiked sample was run per batch to verify the non-existence of ^{233}U in the sample. It is not economical to run spiked and unspiked samples if the samples are known to contain insignificant amounts of ^{233}U. However, it is important to confirm this assumption with each batch.

As outlined in the previous section, the isotope dilution method typically requires analysis of both an unspiked and spiked sample. Table B-5 provides a tabulated summary of all known quantities (and how they are determined) for the isotope dilution calculation for a boron solution. It is assumed that the appropriate chemistry has been performed on the sample.

In this example the spike solution will be referred to as the "mixture". The subscript "spiked" is too easily confused with the "spike" subscript used to distinguish the spike from the sample.

Table B-5: Summary of Spiked and Unspiked Sample Components

Information Type	Quantity	Symbol
Spike		
	Atom % of ^{10}B in spike	$At\%^{10}B_{spike}$
	Atom % of ^{11}B in spike	$At\%^{11}B_{spike}$
	Atoms of the element B added to the sample	B_{spike}
Unspiked Sample		
Measured for unspiked sample:	$^{10}B/^{11}B$ atom ratio	Used to calculate atom percents
Calculate:	Atom % of ^{10}B of sample solution	$At\%^{10}B_{sample}$
	Atom % of ^{11}B of sample solution	$At\%^{11}B_{sample}$
Unknown:	Atoms of B in the sample	B_{sample}
Spiked Sample		
Measured for spiked sample:	$^{10}B/^{11}B$ atom ratio	$R_{mixture}$
Break into components:	Atoms of ^{10}B in the mixture	$= {}^{10}B_{sample} + {}^{10}B_{spike}$
	Atoms of ^{11}B in the mixture	$= {}^{11}B_{sample} + {}^{11}B_{spike}$
Equation		
Expanded $R_{mixture}$ =	$\frac{(At\%^{10}B_{sample} * B_{sample}) + (At\%^{10}B_{spike} * B_{spike})}{(At\%^{11}B_{sample} * B_{sample}) + (At\%^{11}B_{spike} * B_{spike})}$	

The equation in Table B-5 (last row) shows that all quantities are known except for the atoms of boron in the sample being measured (B_{sample}). Thus the $R_{mixture}$ equation can be solved for B_{sample} to calculate the number of atoms of boron in the sample:

$$B_{sample} = \frac{B_{spike} * (At\%^{10}B_{spike} - (R_{mixture} * At\%^{11}B_{spike}))}{(R_{mixture} * At\%^{11}B_{sample}) - At\%^{10}B_{sample}}$$

This approach can be extended for use with elements having more than two isotopes. The resulting equation will be more complicated.

APPENDIX C

EXPERIMENTAL ERROR ANALYSIS

1. Introduction

In a perfect world, all techniques are properly designed and executed; chemistry works perfectly with no human or equipment errors; the instrumentation is properly calibrated and operates flawlessly; and all calculations are complete, correctly executed and reported. However, the complexity of the samples and the demanding quantitative radiochemical measurements result in a 5-10% failure rate[a] no matter how careful the analysis. Furthermore, all successful radiochemical analyses have associated experimental errors. These calculated errors estimate the extent to which the results agree with the actual content of the measured analyte.

This appendix will provide sufficient background for the reader to understand the experimental error analyses that were performed and reported for individual experimental programs. This information includes:

- *background*: definitions, basic statistics as used in these experiments, and additional quality control items;
- *experimental error sources*: provides a summary of each component of the total experimental error;
- *verification of data quality*: what methods were employed to determine the level of confidence in the results and how we quantify them; and
- *end user data usage*: how data are typically used (and misused), suggestions on effective data usage, and lessons learned.

Note that the key word in “error estimate” is “estimate”. The produced data are generated within known probability limits of accuracy and precision controlled by the quality assurance program of the radiochemical analytical laboratory. Do not lose sight of the fact that the actual level of accuracy and precision[b] is not known, only that the precision and accuracy are known to a certain level of confidence. This appendix provides the reader with the necessary tools to follow discussions on the level of confidence for experimental measurements and to use this knowledge for the proper application of the experimental data to scientific studies. The information in this appendix is not a complete discussion of measurement principles, statistical techniques and quality control measures. More detailed information on any topic of this section can be found in the applicable references.

The reader also needs to keep in mind that there are a variety of interpretations for many common statistical terms and subtle differences for terms dependent on the application.This section defines the statistical terms that are used in physics irradiation test program documentationto avoid ambiguity or possible confusion.

2. Background

When assessing any analytical method, one needs to determine whether the conventional measurement method is sufficiently reliable: to what extent are the results accurate or how do

a. Failure is defined here in that no measurement is obtained because of problems during chemical processing.
b. Very often experimentalists think that the precision is a known quantity that can be easily measured. In the pure world of statistics, precision, like accuracy, is an estimate for a finite sample set.

they agree with the actual content of the analyzed component. No measurement method is absolutely perfect and has some degree of uncertainty. Thus it is important to develop methodology to evaluate the data in a way to construct justified conclusions while rejecting interpretations that are not warranted because of the measurements' limitations. Most techniques used in analytical chemistry are based upon statistical concepts. It is beyond the scope of this appendix to provide a complete treatise on statistical methods, their application in experimental planning to obtain the most information from the fewest measurements, and data reduction techniques that ensure that the data's significance is concisely presented. Please note that statistics are not a substitute for the execution of good measurements and statistical methods are most powerful when applied to good data. The following sections will provide the common statistical concepts used in the analytical methods employed for physics irradiation test programs. Please note that the discussion on statistical concepts is from a chemist's view point, not a statistician's.

3. Error Nomenclature

Error refers to the numerical difference between a measured value and the true value. The true value of any quantity is really an abstraction, although scientists believe that they approach it more and more closely as their measurements become increasingly refined. However, the simple truth of the matter is that the true value is never known, thus the true error is not known. If the true error was known, the scientist would merely correct the data. Limits on the true error can be determined and error estimates can be constructed. These estimates are typically referred to as the measurement uncertainty.

Most quantitative analytical chemistry measurements are made using a comparative method. The comparative method is based on the inter-comparison of the sample with a chemical standard. The "true" value of a quantity is known when it is believed that the uncertainty in the measured value is less than the uncertainty in the reference standard with which it is being compared. Chemists will treat chemical standards[c] as "truth," but at the same time they remain skeptical about the standard values because these data do stem from experimental measurements that are performed using techniques that have inherent errors and by human analysts who can make human errors.

To aid the reader in the following experimental discussions, a number of statistical terminologies will be defined in this section. These definitions are used by the majority of the analytical chemistry community and may differ slightly from the purely mathematical definitions or definitions used by other disciplines. It is important for the reader to understand that there is a considerable amount of confusion and interpretation of these terms and that it is always important to clarify what the user means for any given term. For example, one scientist may define standard deviation as the difference between the measurement and the true value, whereas another scientist may define standard deviation as the variation present in any given data set. The reader may disagree with some of the definitions in this section and it is the reader's prerogative. It is not the purpose of this section to debate the validity of the various meanings for statistical terms. This section presents the definitions that will be used in physics irradiation test program documentation so that the reader does not have to "guess" at the meaning of the statistical terminology.

a. Error types

The majority of analytical chemists group error into three different categories: random, systematic and gross. Definitions and examples are provided in the following paragraphs.

c. Also referred to as reference standards and certified standards.

Random (indeterminate) error accompanies all measurements and appear as random fluctuations in the measured quantity and affect the measurement's precision. These errors are typically small. Errors of measurement (i.e. sample weighing, volumetric measurements) are typically random errors. Random errors can usually be corrected by using a mathematical model for the probability distribution of random error which allows assessment of their influence on the final result. Counting is an example of random error. It is a statistical phenomenon and is described by the Poisson distribution. Thus, the random error associated with any counting technique (i.e. radioactive species, ion counting techniques) can be estimated by this mathematical model. If all equipment is operating properly, the smallest error (one standard deviation) for a count rate will be the square root of the count rate. This error is inherent in the system and cannot be eliminated. However, mathematics provides us with a tool we can use to reduce the random error for a given measurement: measure more counts since as the count rate increases, the ratio of the square root of the count rate to the count rate decreases. This approach works in theory provided that there is sufficient sample and time to collect the data, and that there are no other time dependent variations that contribute to the overall error of the measurement. Note that counting statistics are eventually outweighed by other errors and therefore counting forever doesn't work to eliminate the measurement error.

Systematic (determinate) errors are constant in nature and affect the measurement's accuracy. The sources of systematic errors are typically errors of procedure. Systematic errors are sometimes segregated by their origin: methodic, operative and instrumental. A method error relates to the involved chemical systems of the method. An operative error relates to the ineptitude of the experimenter. Instrumental errors relate to a failure of the measuring devices to perform in accordance with required standards. Frequently the source of an error may lie in more than one of these categories. Examples of systematic error are: mis-calibrated instrumentation, a contaminated reagent, or a corrupted standard solution. The analyst can frequently establish the cause of the error and correct it. This type of error can be avoided or at least reduced by effectively designed and executed quality assurance programs.

Gross (blunders) errors are generally mistakes in the analytical process or are caused by insufficient care by the analyst. Examples of gross errors are mislabeling a sample, using the wrong reagent, or a calculation error. Gross errors can seriously affect the accuracy of the final result and sometimes are not revealed by quality assurance programs (especially if the gross error is derived from faulty execution of the quality assurance program). Gross errors typically cannot be established afterwards with the exception being some calculational errors.

There are additional error types that are related to, or are subsets of, the error types defined above. Their definitions follow.

Bias is typically defined as a systematic error that is inherent in a method (weighing errors, extraction inefficiencies) or caused by some artifact or idiosyncrasy of the measurement system (blanks, contamination, mechanical losses, calibration errors). An example of an experimental bias is an improperly calibrated pipette used to deliver a set amount of spike to the sample solution. All analyses will be skewed by the same error in the added spike. For instance, if the error results in delivering 5% more spike solution than expected, the results will be 5% lower[d] than the actual value.

Constant errors are determinate errors that are nearly constant in a series of analyses regardless of the sample size. A process blank is an example of a constant error. This error remains constant for the entire sample set. Since this type of error is not proportional to the sample size, it's impact varies according to the size of the sample. For example, if a uranium blank concentration is 0.0008 grams of uranium per gram of sample solution, this error will have little discernible effect on a measured sample that has a uranium concentration of 13 grams of uranium per gram of sample solution, but considerable effect on a measured sample that has a uranium concentration of 0.002 grams of uranium per gram of sample solution, since the blank correction involves a direct subtraction of the process blank.

Proportional errors are determinate errors that vary with the sample size in such a way that the relative error[e] remains constant. A contaminated reagent is an example of a constant error. The more reagent that is used in the radiochemical procedure, the larger the error in cases where the volume of reagent used varies with the sample size. For example, larger samples require proportionally larger volumes of acid solution to ensure complete dissolution.

b. The accuracy, precision and uncertainty definition conundrum

Accuracy, precision, and uncertainty comprise one of the most mis-understood and misused group of terms used in the engineering community. The confusion is propagated by the fact that most dictionaries do not distinguish between precision and accuracy. These three terms are constantly used interchangeably to such an extent that whenever these terms are used, the reader must determine what is really meant by them. Analytical chemists carefully distinguish uncertainty, accuracy, and precision and their most widely used definitions follow.

Uncertainty is the range of values within which the true value is estimated to lie. It is the best estimate of possible inaccuracy due to both random and systematic error. It seems that this term is frequently used as a catch all phrase. This author has seen the term uncertainty used to refer to the precision of a measurement, the accuracy of the measurement, or a combination of both: these are incorrect usage and should be avoided.

Accuracy is the degree of agreement of a measured value with the "true" or expected value of the quantity of concern. An accurate result is the one that agrees most closely with the "true" value of a measured quantity. Comparison is usually made on the basis of an inverse measure of accuracy: the smaller the error estimate, the greater the accuracy. The error estimate is most frequently expressed relative to the size of the measured quantity as a percent or in parts per thousand. Most often the "true" value of a measurement is not known (that is why the measurement is being performed) and cannot be ascertained. However, the accuracy of the method can be estimated by the measurement of standards and if the experiment is properly designed and executed, the measurement accuracy can be established within a certain degree of confidence. Note that accuracy is the difference from "truth" and not to be confused with how well an attribute is measured (the precision).

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d. The result is lower because the analysis is determined by taking ratios to the spike: the sample to spike ratio is smaller than expected because there is more spike present in the solution than expected. See the main document for details on spiking samples.
e. Relative error is the absolute error divided by the perceived "true" value and serves as a criterion of the accuracy of the result. It is frequently expressed as a percent. Absolute error is the difference between the analytical result and the perceived true value.

Precision is the degree of agreement of a group of experimental results and does not imply anything about their relation to the "true" value. Precision measures the difference from the mean of multiple measurements. It is possible to have precise values that are inaccurate since an error causing deviation from the true value may affect all the measurements equally. Like accuracy, comparison is usually made on the basis of an inverse measure of precision of multiple measurements: the smaller the error estimate, the greater the precision. Precision is also frequently expressed relative to the size of the measured quantity as a percent or in parts per thousand. Sometimes the term reproducibility is substituted for precision which is not incorrect. However, the term reproducibility typically relates to the experimental reproducibility and is typically defined as the mutual agreement of parallel results within slight variations of the sample composition.

4. Statistical Terms

Statistical principles are used to design experimental programs, define and optimize sampling plans, demonstrate statistical control, perform data evaluation and make the wide variety of decisions in the use and the application of the measurements. An in-depth discussion of statistical principles as applied to analytical measurements is beyond the scope of this document. References 9, 10, and 11 are excellent references providing easy to follow discussions using real-world examples. This section will summarize key terms employed in typical physics irradiation experimental programs. There will be no presentation of any equations for these statistical terms. This is done deliberately because although statistical terms are precisely defined, there are a number of subtleties in the equations and in their specific application. Each subcontractor performs statistics in a slightly different way and the reader needs to examine the subcontractor's documentation to determine exactly how data and their variation were calculated.

a. Parent population and distributions

When a measurement is made, it is expected that the measurement should approximate the "true" value of the quantity. If a second measurement is made, there will probably be a discrepancy between the two measurements due to random errors and neither measurement will be exactly correct (i.e. equal to the "true" value). As additional measurements are performed, a pattern will emerge from the data with some measurements being too large and others too small. If systematic errors are small enough to be neglected or can be corrected for, the data should be distributed around the "true" value. The power of mathematics can construct a probability distribution using a parent population for the distribution which assumes an infinite number of measurements. This probability distribution then defines the probability of getting any particular observation in one measurement. The use of these probability distributions for the hypothetical parent population is very useful since only a finite number of measurements can be made for any given experiment. The experimental data points are assumed to be a random sampling of a parent population. There are a number of standard distribution types that can be used to model the random sampling of the experiment. The reader can consult the references for more information on these distributions.

b. Estimated mean

The sample mean is typically defined as the sum of the measurements divided by the number of measurements where the parent population is an infinite number. In real life, only a finite number of measurements are performed and thus the experimental mean is only an estimate of

the actual mean of the distribution. Note that the mean is different from the parent population's median. In the limit of an infinite number of measurements, the median is the value for which half the observations will be less than the median and half will be greater. There is also a term that is the "most probable value" of the parent population which is the value for which the parent distribution has its greatest value. In any given experimental measurement, this is the value that will probably occur most often. The reader should be aware of these other terms. However, for most analytical measurements, the experimental mean is the most commonly employed term.

c. Estimated confidence interval

Since the experimental mean cannot really be expected to coincide with the "true" value, confidence intervals are frequently estimated. The confidence interval is the range of values, calculated from an estimate of the mean and the standard deviation, which is expected to include the population mean within a stated level of confidence. Reported confidence intervals for physics irradiation test program data typically have a stated level of confidence of 95% (95% CI[f]). This confidence interval was estimated by multiplying the standard deviation of the measurement by a factor of two. The standard deviation provides a measure of the variation present in a data set. The standard deviation is frequently estimated by making a number of replicate measurements for a given sample. The standard deviation[g] is then calculated as the mean square deviation of the measured values from their mean. The equation for standard deviation can be found in statistic books or in manuals for calculators and spreadsheets. The equations may differ by the denominator which is typically either the number of measurements, or the number of measurements minus one, the latter being the correct approach in almost all experimental situations.

The majority of the confidence intervals for physics irradiation test programs are described by two-sided intervals. However, in the case where minimal detection limits are reported, it is typically described as a one-sided bound. This appendix will not cover one-sided bounds, the reader can refer to the designated references and additional details on detection limits can be found in Appendix D.

d. Significance testing

Statistical methods can be used to perform significance testing to help the experimenter analyze the reliability of the measurements. Examples of some experimental measurement questions are provided in the following bullets.

- Do two estimates of precision differ?
- What are the confidence limits of an estimate of a standard deviation?
- Does a measured value differ from the expected value?
- Do the means of two measured sets of values disagree significantly?

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f. Also referred to as 2σ error

g. Some scientists use the standard error which is the standard deviation divided by the square root of the number of replicates. This estimates the variability in a sample mean, which is smaller than the variability in individual measurements. Of course, when only a single measurement is available, it is not possible to reduce variability via averaging.

Statistical methods are used to objectively construct rejection criteria to identify outliers that should be subject to careful scrutiny. These methods can be found in any basic statistic book. Sometimes problems with experimental methods or data reduction are uncovered that provide legitimate justification for deletion of outliers. Very few statistical methods have been employed in recent physics irradiation test programs since there was an insufficient data population for many of these methods to be appropriately applied.

e. Propagation of errors

The estimates for the mean and standard deviation for a set of measurements describe the desired result and the uncertainties of the data set. Many of the measurements performed for physics irradiation test programs are not single measurements, but a series of measurements, each with its own associated error estimates. Thus the estimated experimental uncertainty is a compilation of all estimated uncertainties for all parameters (measurements and processes) that are performed to provide the final answer. The collective random uncertainty in the result is determined using the standard deviations[h] of the individual parameters. This process is referred to as the propagation of errors. Some standard formulas for propagation of errors can be found in Appendix B.

Standard deviations are frequently not available for all the measurements performed for a given analysis. In these cases, there may be available error estimates. For example, the manufacturer will provide a tolerance on an analytical balance used for weighing. Other times the uncertainty is not known. In these cases historical estimates are used and sometimes educated “guesses” derived from years of experience are employed. This is not a satisfactory source for the measurement error estimates, but in some cases it provides the only available estimate.

f. Significant figures

Significant figures imply the precision of an experimental result. For any measurement, the number should be provided with as many digits as are significant. The number of significant figures is all digits between the least[i] and most[j] significant digit. Using this definition, 235.1, 0.000002351, 235.100, 2.351×10^{-8} and 2351 all have four significant digits. The measurement of how many digits are significant is dependent on the measuring device. A micrometer provides a length measurement more precisely (thus with more significant figures) than a standard ruler. In the age of computer generated data, very often measurements are reported with “extraneous” significant figures. For example, a digital voltmeter can read to 1/10,000 of a volt (0.0001). The reported ratio of two voltage measurements printed by the software is 1.948567039. This result has extraneous significant figures and should be reported as 1.9486 V (volts). It is appropriate to carry extraneous significant figures to minimize round off errors. However, final results need to be provided in the correct number of significant figures to avoid misleading the user on the measurement’s precision. Furthermore, when performing calculations, the number of significant figures in the final value is dictated by the value having the least number of significant figures. For example, if the above ratio is multiplied by 0.225, the result should be reported as 0.438 V.

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h. When they are available.
i. The right-most digit if the number contains a decimal point, the right-most nonzero digit if there is no decimal point.
j. The left-most nonzero digit.

g. Round off error

Round off error can occur due to truncation of digits from a numerical value, or when insignificant digits are dropped from a number and the last retained digit is not properly rounded off, or rounded off using a different method than typically employed by analytical chemists[k]. To properly round off a number, the number is truncated to the number of significant digits and the excess digits are treated as a decimal fraction. If that fraction is greater than 1/2, the least significant digit is incremented; if the fraction is less than 1/2, the least significant digit is not incremented; and if the fraction equals 1/2, the least significant digit is incremented only if it is odd. Round off errors can result in the inability of the user to exactly reproduce the subcontractor's results using the provided raw data. It is common that the computer program is carrying numbers to a larger number of significant figures than printed out in the data report. It could also occur that one analyst may hand calculate numbers off the data reports and another analyst uses a computer program. Users should be aware of this phenomenon since it can cause differences in the final results.

5. Definitions for Other Commonly Used Terms

The following is an alphabetical list of additional terms that may be used in physics irradiation test program documentation and are provided here for the reader's convenience[l].

Absolute method: a method in which characterization is based entirely on physically (absolute) defined standards.

Certified value: the value on the certificate that is the best estimate of the value for a property of a reference material.

Check standard: a standard used for physical calibration and is measured periodically. The results are plotted on a control chart to evaluate the measurement process.

Comparative method: a method which is based on the inter-comparison of the sample with a chemical standard.

Confidence level: (also referred to as level of confidence) Accuracy and precision are characteristics of actual measurement process. Typically, the true accuracy and precision are not known exactly, but are estimated. "Confidence" level refers to the level of certainty with which the accuracy and precision are estimated.

Control chart: a plot of test results with respect to time or measurement sequence, together with the limits within which they are expected to lie when the system is in a state of statistical control.

Control limit: the limits shown on a control chart beyond which it is highly improbable that a point could lie while the system remains in a state of statistical control. If values fall outside these limits, an investigation to identify the cause will be initiated and no additional samples will be processed until the cause is identified and eliminated.

Control sample: a material of known composition that is analyzed concurrently with test samples to evaluate a measurement process.

Detection limit: the smallest concentration/amount of species of interest that can be measured by a single measurement with a stated level of confidence.

k. Spreadsheet applications are famous for doing this.
l. The majority of these definition are reproduced from Reference 8.

Duplicate measurement: a second measurement made on the same (or identical) sample of material to assist in the evaluation of measurement variance.

Outlier: a value which deviates markedly from the values of the other members in the population.

Primary standard: a substance that has an accepted value (within specific limits) and is used to establish the value of the same or related property of another material. Note that a primary standard for one purpose may have been a secondary standard for another.

Reference material: a material or substance that has one or more properties that are sufficiently well established to be used for the calibration of equipment, the assessment of a measurement method, or for the assignment of values to materials.

Reference method: a method which was been specified as capable, by virtue of recognized accuracy, of providing primary reference data.

Replicate: a repeat measurement of a sample. The reported number of replicates typically includes the original. For example, three replicates is defined as the original measurement and two additional repeat measurements.

Routine method: a method used in recurring analytical problems.

Secondary standard: a standard whose value is based upon composition is based upon a comparison with a primary standard. Note that a secondary standard for one purpose may have been a primary standard for another.

Selectivity: the ability of the instrumentation (or methodology) to respond to the desired analyte or constituent and not to others.

Sensitivity: the capability of instrumentation (or methodology) to discriminate between a sample having differing concentrations or containing differing amounts of the analyte.

Standard: a substance having properties to be known with sufficient accuracy to permit its use to evaluate the same property for another sample. In chemical measurements, it is a solution commonly prepared by the analyst to establish a calibration curve for an analytical instrument.

Standardization: the process where the value of a potential standard is fixed by its measurement with respect to a standard of known value.

Standard method: a method or procedure developed by an analytical organization and is based upon consensus opinion or other criteria and is typically evaluated for its reliability by a collaborative testing procedure.

Standard reference material: a reference material distributed by a number of vendors that has been certified either by direct or indirect comparison to a known standard typically provided by the National Institute of Standards and Technology[m] (NIST).

Traceability: the ability to trace the source of uncertainty of the measurement or a measured value.

m. Formerly designated as the National Bureau of Standards (NBS).

6. Experimental Error Sources

Measurements of uranium, transuranics and fission products are typically compared to calculated values derived from physics model calculations. Often the only quoted uncertainties on the measured data are the errors associated with the analytical measurement. However, the analytical measurement uncertainty is only one source of the total uncertainty for the entire experimental evolution. The total experimental uncertainty for typical physics irradiation experiments is comprised of three components:

1 variations in the pre-irradiation compositions,

2 the sampling variability (induced by specimen collection procedures), and

3 the measurement uncertainties.

The measurement uncertainties are typically the most readily available since they are provided by the subcontracting laboratory. The other two components are sometimes very difficult to quantify. As a result, some analysts may only use measurement errors since they are readily available, and it was too difficult to quantify the other two error components. However, the end user must realize that using the measurement uncertainty alone can be misleading since it is typically the smallest contributor to the total experimental uncertainty for these types of experiments. These error components are reviewed in the following paragraphs.

a. Pre-irradiation composition uncertainties

It is important to know the uncertainty in the composition of the test specimen prior to irradiation. Not only does the uncertainty in the uranium concentration need to be known, but also the uncertainty of the spatial distribution of uranium throughout the test specimen[n].

It is important to know if there are trace quantities of any of the measured nuclides of interest in the test. Many of the nuclides are produced in very small quantities in comparison to the major sample constituents. Thus, a small amount of impurity in the sample prior to irradiation can adversely affect the results if not corrected for. Impurities can also produce nuclides that may not be measured, but that interfere with the analytical measurement.

b. Sampling variability

The sampling process is not perfect and there is an uncertainty associated with this evolution. This sampling uncertainty is a component of the overall experimental uncertainty. Another possible sampling error is uncorrected systematic error due to contamination.

c. Measurement uncertainties

This document covers the numerous sources of errors that can be made in quantitative radiochemical analyses and will not be repeated here. The quality assurance program for the analytical laboratory should cover all of these issues, but it does not always account for human error and/or sloppiness, and uncontrollable confounding factors that may affect results (e.g. difficult to establish and/or maintain chemical equilibrium, environment variables such as ambient temperature and humidity, operator-technique effects, reagent batch effects). In addition, the quality within any given laboratory at any given time can change.

n. Typically test specimens are constructed to have a uniform uranium distribution across the entire sampled volume

For the process described in a typical physics irradiation test program, the total experimental uncertainty can be calculated by propagating the three error components (after determining the correct way to combine all of the error components).

7. Verification of Data Quality

The purpose of the physics irradiation test programs is to provide measurements for irradiated samples. Because of the nature of these samples, the "true" value is unknown. However, the values are frequently known approximately (to the correct order of magnitude or better) for many of the measurements, either from other related experiments, from theoretical calculations, or other experimental approaches. There were also systematic ways to determine the quality of the data from the data themselves.

A variety of methods can be used to determine experimental quality and the confidence in the experimental results. Evaluation of data quality is a function of how much is known for any particular sample and the employed methods used for analysis. All of this information needs to be examined in totality to determine the quality of any particular analysis. Some methods for data quality verification are summarized in the following paragraphs.

a. Comparison with the known composition

This is the ideal comparison, but in these experiments, this quantity was what was being measured. However, this method was used by the subcontractors when examining standard and control samples that were performed as part of each laboratory's quality assurance program. Each laboratory was required to provide the analysis certification for all of their reference standards and provide analyses for comparison to these values. These materials were examined to determine the ability of the laboratory to reproduce the certified values and to also assess the suitability of the control standard to represent the samples to be analyzed (concentration, isotopic abundances, etc.). These data provided a level of confidence that the instrumentation was calibrated and functioning properly and/or that the separation chemistry was working as expected.

b. Comparison to the expected value

This is a good comparison if there is a high level of confidence in the expected value. For most physics irradiation test programs, the measurements are compared to calculated values (where available) derived from diffusion theory model predictions. One would question the use of these calculations to provide the expected values since the experiment is being performed to verify the accuracy of the diffusion theory model calculations. However, the collective body of physics irradiation test data has shown that the physics model calculations can predict over ninety percent of the analyses with errors of 5-10% (unless there were gross irradiation parameter errors). The use of calculated expected values is a good reasonableness check to determine the validity of the experimental measurements. However, one must understand the limitations of the physics model predictions and how they may provide good expected values for some (but not all) measured nuclides for some test specimen types, but not in others.

Physics models cannot exactly model the test specimens. For example, the model uses nominal starting materials, does not include all trace impurities and does not track all production and decay chains. There is uncertainty in the basic nuclear data employed in the models such as cross section data. Some cross sections are strongly energy dependent in the

thermal neutron energy range. The irradiation parameters need to be precisely known and modeled since the neutron flux in the test reactor is spatially and time dependent.

c. Examination of the analysis of comparable samples

Examination of how well a subcontracting laboratory can reproduce results for a well characterized sample comparable to those to be measured provides a high level of confidence in the laboratory's ability to provide good data for the sample to be analyzed (referred to as "unknowns'). This well characterized sample is typically referred to as a "surrogate" and is defined as having the same composition, the same physical characteristics, and undergoing the same processes as the unknowns. It is relatively straightforward to construct standards for some experimental programs. For example, consider an experiment where the goal is to determine the trace element contents for chromium, iron and calcium in a set of solutions. A suite of standard solutions could be created by adding precisely measured amounts of chromium, iron and calcium to a pure solution having the same composition as the set of solutions to be analyzed. These standard solutions of known concentration would be provided to the subcontractor and their results compared to the known concentrations. However, as described in the previous paragraphs, the sample characteristics of the irradiated material are very complicated and cannot be effectively simulated by a manufactured standard. Mock-up samples can be constructed to investigate certain characteristics of the sample, but at the time of the writing of this document, there is no good standard that mimics all characteristics of the irradiated test specimens. Unirradiated test specimens can be used as a surrogate, but it has not undergone irradiation which results in changing the composition of the material (i.e. uranium depletion, buildup of fission products and transuranics) and also the physical properties (i.e. radiation damage that changes how the sample dissolves). The subcontractors did construct various mock-up solutions to check out certain aspects of the chemistry. However, these mock-ups, although useful, were simplistic and had a limited number of attributes of the actual samples which are comparatively complicated in their composition.

d. Examination of the measurement precision

It is always desirable to obtain a measurement with excellent precision. However, the precision very often only conveys the reproducibility for a single measurement. It is possible to have a very precise, inaccurate number due to a systematic error. Examination of the precision of the measurements does provide some information on the data quality. The precision usually is a good indication of the quality of the instrumental analysis. However, poor precision may not be an indication of an instrumental analysis, but a result of a low count rate. Low count rates themselves do not imply an instrumental problem. It could imply that the chemical yield was poor or just that there was very little of the species of interest present in the sample and the sample should not have been diluted to the current concentration. Abnormally low count rates should be investigated to assess the probability of a problem with the methodology. However, there are other possibilities such as the fact that the species has effectively decayed away due to the extended time between end of irradiation and the time of measurement.

e. Examination of the measurement accuracy

It is always desirable to obtain a measurement with excellent accuracy. However, it is important to know how the accuracy was determined. If the accuracy of a method is

determined by analysis of a control, it is possible that an experimental issue affects the separation of the unknown sample and the accuracy is affected without a direct measurement of that effect.

f. Examination of the statistics for a collection of samples

Examination of a group of measurements, particularly if the data set is comprised of exact replicates, can be more enlightening than examination of a single value. However, in the absence of replicates, examination of a number of different analyses for the same sample can be very useful in data quality evaluations. For example, having key fission product and transuranic data in addition to uranium contents can be very useful in determining if the data collection makes physical sense: a sample having greater uranium depletion should also exhibit a larger amount[o] of fission products and transuranics than a less depleted sample.

g. Examination of comparable data sets performed by different laboratories

Comparison of a measurement data set for multiple samples analyzed by different laboratories is a useful tool in examining data quality. If all laboratories provide the same numbers within experimental uncertainties, there is a high level of confidence in the results[p]. However, if they provide significantly different results, it is very difficult to determine which analyses is the correct one. This situation makes it difficult to troubleshoot where the experiment went wrong.

8. End User Data Usage

The end user of the data must take care to examine the experimental uncertainties of the reported data and how they may affect the data application. This section provides some comments on end user data usage and some observations that have been made examining the historical use of experiment data from physics irradiation test programs.

- Don’t forget that the real samples are not “nominal” prior to irradiation and evaluate how manufacturing tolerances (compositions, positioning, physical dimensions, etc.) affect the data application. This includes what is not known about the sample (i.e. trace element contents that are not provided).
- Be mindful of the data attributes and how they match up with the calculated values – perform proper decay corrections (including production modes because a nuclide may be a daughter of another nuclide’s decay), compare the correct volumes, compare at the correct positions, and use the proper units.
- Although it is a habit of end users to look at individual data points, comparison by nuclide is sometimes not the best approach. Examine the data comparisons as a function of depletion. Examine the entire group of analyses for each test specimen to identify inconsistencies that would point to experimental issues. Be creative and use “physical” common sense.
- Note that test specimen weights can be a misleading parameter for the measurement of uniform test specimen dimensions. For example, manufacturing allowances can account for a variability of up to 6% in test specimen weight without changing the test specimen dimensions: do not normalize the data using the test specimen weights in this case.

o. Ensure that corrections for decay and build-up have been performed.
p. There is always a possibility that all the laboratories are wrong. However, this is an improbable event especially when laboratories use different methods since there can be inherent biases in a particular method.

9. Summary

It is important to remember that the measurement accuracy can never be guaranteed and that the accuracy is judged experimentally by verifying the method by means of an analysis of a substance of precisely known composition. All experimental uncertainties need to be considered when employing the data for any given end use.

Always clarify the terminology used by the reporting laboratory to determine the identity of reported error estimates and check how those estimates were derived. Differences in interpretations of statistical terms can lead to significant confusion.

Typically over 95% of the experimental data will agree well with physics model calculations. But for the small percentage of data that does not agree, the end user needs to dig deeper into the experimental data and how they were measured. Very often the end user is concentrating on explaining a single value for a given sample. This is very difficult due to the uniqueness of the samples. Most often, verification of data quality involves examination of a group of analyses to provide more information on the process. The ability to assess data quality is directly related to how much is known about the experimental process and the sample (both sample composition prior to irradiation as well as end of irradiation measurements).

APPENDIX D

RADIOCHEMICAL ANALYSIS: PITFALLS AND ENLIGHTENMENTS

1. Introduction

Physics irradiation test program samples are very challenging to analyze due to their composition, the number and the variety of analytes, and low analyte concentrations. Sample processing is further complicated in that the samples are radioactive and are physically classified at certain points in the process. Additionally the data may be individually classified and most certainly classified as a data collection. This work is very difficult and requires not only a laboratory with all the proper equipment and facilities, but also experienced personnel to perform the work. These experienced personnel need to be well versed in traditional radiochemical separations and understand the ins and outs of the chemistry for a wide variety of analytes, some of which are very difficult to separate from the major constituents and/or each other. This expertise is becoming scarcer as instrumental analysis is replacing many wet chemical methods. Instrumental analysis has improved, but at this point in time, still cannot replace the necessity to perform separation chemistry prior to analysis.

Information specific for physics irradiation test program samples are provided in an attempt to chronicle the problems and challenges that scientists have encountered in over 30 years of processing these samples. This appendix cannot be inclusive of all issues, but attempts to gather the remaining knowledge of program radiochemists who have not yet retired. The author has hands-on expertise in only one facet of radiochemical analysis and has limited knowledge in others. Thus, the depth of information for each area relies on the contributions of the remaining experts who have hands-on experience processing these unique and challenging program samples.

The field of radiochemical analysis, as in any scientific or technological field, is rapidly evolving. Some of the details of the techniques and instrumentation covered in this document are now outdated. For example, new ICPMS instruments use dynamic reaction chambers to literally blow apart molecular interferences so that the issue of molecular interference will no longer be as big of a concern. However, the information captured in this document is pertinent to the experiments already performed and can be applicable for on going or future experiments performed by laboratories owning older instrumentation. The underlying principles of good sample preparation and analysis will never change in that the methods need to be appropriately designed and executed with appropriate quality assurance measures.

2. Prerequisites

This appendix will not reiterate the material already covered in this document. The reader should review that material prior to reviewing this appendix. This appendix also does not document the step by step procedures for each analysis since they differ between experiments.

The test sponsor responsible for administering these experiments does not have to be an expert in all the analyses. However, it is important for the test sponsor to be aware of the sample processing idiosyncrasies and to forward the program specific information to the subcontractor performing the analyses.

3. Appendix Organization

This appendix is organized into topical categories. The issues for processes that deal with the sample as a single entity are reviewed first, followed by information organized by the measurement technique. Information for each analyte is provided for each measurement technique. Some analytes are measured using more than one technique and will appear under multiple technique headings. This appendix's topics are as follows:

- Regulatory and Administrative Issues
- Security Issues
- Experimental Methodology Issues
- Quality Assurance Issues
- Dissolution Process Issues
- Radiochemical Separation and Purification Techniques
- Radiochemical Carrier Chemistry
- Instrumental Analysis Techniques (Overview)
- Alpha Spectroscopy Technique
- Beta Counting Technique
- Gamma Spectroscopy Technique
- Thermal Ionization Mass Spectroscopy and Isotope Dilution Technique
- Inductively Coupled Plasma Mass Spectrometry Technique
- Inductively Coupled Plasma Atomic Emission Spectroscopy Technique
- Errors in the Data Reduction Process
- The Complicated World of Nuclear Physics
- Test Specimen Composition Impact on Experimental Methodology
- So What Happens When Things go Wrong?
- Summary

Note that several non-technical categories are included. The test sponsor is primarily responsible for the experimental technical issues. However, many administrative issues can impact the science and have an adverse impact on the experimental results. The test sponsor needs to be aware of these issues and ensure that personnel in support functions such as shipping, security, etc. are properly educated on the experimental requirements as they relate to the support personnel's area of expertise. Communication is a key factor to the experimental program's success and it is the responsibility of the test sponsor to keep track of all the disciplines involved in execution of the experiment.

4. Regulatory and Administrative Issues

This section discusses issues that are not technical in nature, but can impact experimental programs by affecting the ability to ship samples, process samples by a certain methodology, dispose of samples, and affect other facets of the experimental process. Parts of the experimental process that were routine and accepted one year, will turn into show-stoppers the following year. Federal and state regulations are constantly changing and some of these changes can potentially have a dramatic effect on experimental program execution. The test sponsor needs to keep in touch with experts in these areas to avoid an unpleasant "surprise" that may hold up shipping, change radiochemical methods, or drive some other change that can impact the schedule and/or the science of the experimental program.

In the commercial industry, there are federal mandates which are constant across the country (usually under the cognizance of the Environmental Protection Agency (EPA)), and there are state mandates that will vary from state to state. For laboratories that are run for the Department of Energy (DOE), there is an additional layer of federal mandates in addition to those administered by the EPA. In addition to federal and state mandates, there are also local site mandates. The term "administrative" is used in this section to refer to the local interpretations of the mandates for any given site. All of these administrative and regulatory issues can change at a moment's notice.

a. Shipping

The irradiated test specimens are solid samples and are packaged as dictated by the irradiation facility. Many situations can impact the shipping and are enumerated in this section. Note that this is not an inclusive list of all possible situations that can impact shipping: they are the main ones and/or ones that have affected past shipments.

Resource availability (hot cells, equipment, container, manpower, trucking company availability) at the irradiation facility can delay shipments. A work stoppage for any reason, or higher priority emergent work, can delay the packaging and loading of the samples. Sample integrity is also an issue. Since the samples are stored in the water pit, if they accidentally become wet, they are compromised and cannot be used. Even if wetting did not adversely affect sample integrity, the samples loaded into a container cannot be shipped if wet. Drying a sample that has potential loose contamination is typically not attempted.

Shipping container contents need to be characterized for compliance with the Department of Transportation regulations. In addition, a detailed curie estimate needs to be provided to the receiving laboratory for shipment receipt purposes (i.e. it is used to construct the nuclear safety analyses). The content of this curie estimate does not necessarily stay the same year to year. For example, for years, the irradiation facility sent curie estimates to one subcontractor for the receipt of radioactive samples. The requirements were that the originating laboratory provided curie estimates for any constituent that comprised 1% or more of the total radioactivity of the sample. The subcontractor changed the requirements without notice to include 95 additional nuclides as provided in Attachment 1 of DOE-STD-1027-2. The required information was not readily available and new calculations needed to be constructed to provide the requested information. If the shipment had not already been delayed for shipment due to problems at the subcontractor's laboratory, the shipment would have been delayed awaiting the curie estimate data.

The receiving laboratory needs to be certified in the handling and unloading of the container. This process can be affected by issues similar to those that can holdup the packaging of the samples:

resource availability, equipment breakdown, etc. For example, one shipment was delayed for months due to an industrial accident that resulted in a fatality. The entire laboratory stopped work and everyone underwent special training. In the meantime, the overhead cranes went out of certification and, after the personnel training was complete, had to be recertified before the laboratory could unload the cask. Another example is a radiochemical laboratory that was completely shutdown because of a radioactive release. This was not an active subcontractor for current physics irradiation test program work, but illustrates how non-technical issues can impact experiment execution. This is one of the drivers for having two qualified subcontractors for this type of work.

Other surprises can impact shipment: an incident or failure involving the same type of shipping container may result in the suspension of all containers of that type until the situation is investigated. State regulations can change and deny access to certain public highways for radioactive shipments. Certificate of compliance can expire and other issues can affect the process. Currently we cannot ship a particular cask due to containment issues requiring government approval of each shipment.

The existing casks available for shipping program radioactive materials from the current irradiation facility cannot be used to ship liquid samples: all samples must exist as a solid.

b. Waste stream

It is useful to define several terms prior to the discussion of the waste stream generated by the processing of program samples. The following are definitions of the "nasties". Hazardous waste is a combination of waste that because of its characteristics may cause or significantly contribute (or have the potential to significantly contribute) to a human health problem or have a detrimental effect on the environment. A mixed waste is one of the worst types of waste to manage in that it is a waste that is both hazardous and radioactive[a]. A specific type of radioactive waste that has more stringent waste management constraints is transuranic (TRU) waste; that is, waste primarily generated from the research and production of nuclear weapons, but also refers to any waste sample that contains transuranic elements (most commonly plutonium) above the regulatory limits. A mixed waste containing plutonium is the most difficult to manage. The Resource Conservation and Reclamation Act (RCRA) allows the EPA to develop and enforce hazardous waste management regulations[b].

So, how can these various waste categories affect sample processing? Some laboratories do not have an established waste stream for all types of waste. In order to process samples, the laboratory will need to establish the waste stream. The laboratory may change how they process the samples to change the characterization of the waste. The process change could potentially compromise the quality of the results. An unfavorable audit of waste management execution can freeze a laboratory's ability to generate additional waste until the issue is resolved. This could result in a possible suspension in the sample processing. A suspension in the processing can jeopardize the results, especially if one of the analytes is a short lived nuclide that will decay away prior to analysis. A facility may have a low capacity for waste storage. Storage of any on-site waste,

[a] Note that often the term "mixed hazardous waste" is used for mixed waste. That usage is redundant: waste is by definition either mixed or hazardous.
[b] This also applies to greater than Class C waste of any kind. There is an added complication that the NRC controls the regulation for shipping of greater than Class C waste to commercial disposal sites and the DOE has its own rules. Also the DOE is ultimately responsible for all greater than Class C waste, commercial and governmental.

especially mixed or hazardous, is becoming very unpopular due to the liability. When their tanks are full, some laboratories will suspend all radiochemical work until the tanks are emptied. Regulations may change and the waste can't be shipped until waste management procedures are revised. At times, regulations will be changed without the appropriate foresight to determine how compliance can be administered in "the real world." Procedures then need to be developed and approved by the governing agency and this process can take months. There may be only one location for disposal of a certain type of waste (i.e. the Waste Isolation Pilot Plant (WIPP) is currently the only site that is approved to receive defense related TRU waste). A problem at the site could result in it temporarily being unable to receive waste.

The following are some examples of waste issues that directly impacted analyses:

- There are several sample constituents that are RCRA regulated and the radiochemist needs to keep solutions dilute enough to allow the sample to be handled as non-RCRA. Two such elements are chromium and silver which are present in very small amounts in the samples. This is why it is imperative for the radiochemist to be provided approximate ranges for sample constituents as discussed in Section III. This information allows the radiochemist to select the appropriate amount of solvent to keep the concentration of RCRA regulated components below the regulatory limits[c]. Also note that a solution with a pH of less than 2 is considered hazardous, although neutralization can be done fairly easily under the law. Nitrates are more difficult to deal with since they are regulated as oxidizers[d], but the regulations do not straight forwardly define the regulated concentration limits.
- The sulfate dissolution process was suspended at one subcontractor's facility because of the corrosion of their chemical waste tanks. Sulfates accelerate corrosion. The subcontractor used the sulfate dissolution process during the years that the uranium recovery program was in operation. Addition of a small amount of sulfate to the tanks was not a problem because the volume of waste generated in that process was small compared to the amount of waste generated by a large scale uranium recovery program. The laboratory waste was literally a "drop in the bucket". However, once the uranium recovery program was discontinued, the laboratory waste became the "bucket" and there was no longer a dilution effect by the uranium recovery program waste. This is the administrative reason the subcontractor changed their dissolution chemistry from the very successful sulfate dissolution to a nitric acid dissolution which needed addition of hydrofluoric acid for complete sample dissolution. As previously discussed, any excess of fluoride can result in fluoride precipitation of a number of transuranics and fission products.

c. Radiological controls

The fact that the samples are highly radioactive impacts where and how the samples are processed. All subcontractors used to process physics irradiation test program samples are contracted by the DOE. How any given laboratory designs analysis of radioactive samples is dependent on their implementation of the DOE radiological controls mandates. Because of differing interpretations of

[c] Chemists are no longer allowed to get rid of waste by diluting the sample so that it contains hazardous component concentrations below the regulatory limits: dilution is no longer the solution. Any process that dilutes a sample for a non-scientific reason is considered to be waste processing and thus the chemist cannot perform that evolution. Dilution for a scientific reason, such as using enough reagent for dissolution, or to dilute a sample for preparation for instrumental analysis, is allowed. Since subsequent dilutions of the parent solution will be made for the various analytical methods, it is valid to prepare the parent solution dilute enough to keep below the RCRA regulatory limits.

[d] Concentrated nitric acid is a considerable oxidizer and sodium nitrate is explosive.

these mandates, the subcontractors will sometimes handle samples in a way that is very different from the originating laboratory. A question has been asked: "how can they break the rules?" They are not: their implementation of the DOE mandates differs from that of the originating laboratory, but their implementation still complies within the DOE mandates. Most national laboratories are willing to accept a bit more potential "risk" in their handling of radioactive material, but they still comply with their local exposure limits which are comparable to those of the originating laboratory. As-low-as-reasonably-achievable (ALARA) is adhered to across all DOE laboratories, but the definition of "reasonably-achievable" is not exactly defined and thus open to interpretation. What is "reasonably-achievable" in a laboratory that handles small amounts of low level radioactive material is not "reasonably-achievable" in a facility that processes hundreds of pounds of high level radioactive material.

All laboratories will minimize exposure and they will do this in a variety of ways. Highly radioactive solutions will be handled in a hot cell or shielded glove box. Sometimes the sample is processed to remove radioactive constituents that will not be analyzed. This has to be done carefully so that the processing does not accidentally remove species to be analyzed or that the sample will be changed in a way that will compromise any downstream analyses. Samples are often diluted so that the radioactivity of the diluted solution is low enough to allow moving to a lower radiation area with less stringent handling requirements. It is much easier to process samples on the bench top wearing gloves than in a hot cell using manipulators.

Administrative issues can impact how samples are processed. For example, a subcontractor may place restrictions on a given laboratory or instrument. If a laboratory needs to run non-radioactive samples for trace elements on a particular instrument, they may restrict its use to only non-radioactive samples. An instrument may not be used to measure radioactive samples because components where radioactivity can build up with time are not disposable and results in contamination of the instrument. Many laboratories will have two instruments: one to process radioactive samples, and another for non-radioactive samples. However, cost reduction is changing this practice in some laboratories.

Usually radiochemical procedures can be altered to reduce personnel exposure without adversely affecting the data quality. Occasionally, an alteration can be detrimental to data quality. For example, at one laboratory, administrative requirements drastically lowered the local limits for alpha emitters. This situation resulted in a dramatic change in the spiking of burn-up samples. The burn-up samples were spiked using ^{233}U which has a high specific activity. Thus, in order to be able to remove the processed spiked sample from the hot cell, the amount of ^{233}U spike was significantly reduced. This change resulted in a spike to ^{235}U ratio of one to twenty. As previously mentioned, the ideal ratio is one to one. This situation resulted in a decrease in the accuracy for low abundance uranium isotope measurements.

d. Miscellaneous

There are situations when a laboratory will decide not to use a particular reagent due to the risk, administrative constraints, or the supplier stopped making the chemical because of the environmental (and/or legal) liability. Chemical reagent substitution can impact the effectiveness of a successful, well established method. For example, when barium and chromium became classified as hazardous (constituents that would make their use with radioactive samples produce mixed waste), those procedures that utilized barium chromate were required to be changed.

A significant change in facilities can impact a subcontracting laboratory's ability to process program samples. Hot cells have a very high overhead – even when they aren't being used. To cut costs, many laboratories have shut down and some have even dismantled their hot cell facilities. Regulations tighten as a function of time and it becomes more difficult and more expensive to decommission highly radioactive facilities (especially since most have significant TRU contamination). Some subcontracting laboratories have good analytical radiochemistry laboratories, but have lost the ability to receive and unload current physics irradiation test program shipping containers.

Significant changes in analytical laboratory resources (both personnel and equipment) can impact the subcontractor's ability to process program samples. Some laboratories depend on the expertise of a single radiochemist, and when that radiochemist changes jobs or retires the expertise is lost. Reorganization of a facility can rob the analytical laboratory of their talent and their abilities are decreased until they can find replacement personnel. Rising costs have resulted in some laboratories retiring instrumentation that is expensive to maintain. Significant changes can also have a positive impact. For example, Oak Ridge National Laboratory has spent over three million dollars in upgrading their equipment with state-of-the-art instrumentation which could improve their current abilities. Addition of new scientists can also result in an increase in the quality of the results.

5. Security Issues

One key item is the role of the test sponsor as an educator to help the laboratory design their security plans for any program involving classified samples and/or information. The security plan needs to adequately protect the samples and associated data without implementing excessive security measures that do not provide any extra protection, only make sample processing more cumbersome and time consuming. These unnecessary security requirements waste resources that can be used more effectively in sample processing. The test sponsor needs to have working knowledge of the security issues relating to the experimental samples and the generated data to appropriately interface with the security community. The test sponsor does not have to be an authorized derivative classifier (although it could be very convenient), but needs to read the security guidelines specific to the samples and data. This also ensures that the test sponsor properly interfaces with the subcontractor in any discussions and/or data transmissions in an unclassified format. It is also important for the test sponsor to insure that classified information is properly controlled and that access to all information is on a need-to-know basis. Need-to-know limits the amount of information and the number of persons who receive that information. The information is restricted to the people who require the information to perform their work and to prevent access by persons who do not need the information. Proper need-to-know controls minimize the extent of damage that any one person can inflict by inappropriately revealing information.

6. Experimental Methodology Issues

The radiochemical processing of program samples is very difficult, even for a laboratory that has previously processed these samples. New subcontractors believe that they understand how to process irradiated samples, but the composition of these samples make them more challenging than expected. The high concentrations of some major components make the samples difficult to process, especially since the analyses involved very trace amounts of the analytes.

The experiments are very complex and problems can arise if an experiment is only viewed as a series of independent pieces. Many analyses are inter-connected and comprised of interactive processes. A change in one part of the experiment can ripple across other analyses. For example, the use of excess hydrofluoric acid (HF) to dissolve an irradiated uranium sample can cause the precipitation of rare earth and transuranic elements of interest by co-precipitation. The sponsor should acquire a chemistry overview of the process by having the subcontractor produce a flowchart of the overall experiment. Although the subcontractor should do this as a part of their quality assurance program, many will only provide flow charts for the individual pieces of the experiment usually grouped by technique. A flowchart of the entire process will force the subcontractor to assess all processes and their inter-dependencies.

7. Quality Assurance Issues

Section VIII[e] provided background information on quality control for radiochemical analytical laboratories. Quality assurance programs define what methods are used to determine how good the experiments are and documents the level of confidence in the results and how they are quantified. Section VIII also covered reference materials and blanks in detail and summarized the many components to quality control. A complete discussion of these topics is beyond the scope of this document. However, this section will discuss a few more components of quality control as well as provide additional details on reference materials and blanks.

a. Sample management

Good sample management is imperative to ensure high quality data. If samples are switched, or contaminated prior or during analysis, the resulting data are adversely affected.

- Maintaining correct sample identification is a critical item and an issue that can most easily be compromised due to human error. It is relatively easy to switch or mislabel a sample vial[f]. Oftentimes a sampling error can be suspected of occurring, but it is often an unrecoverable error.
- It is important to control how the samples are handled and what things come in contact with them. For example, if the solid samples come in contact with water (i.e. leaking container stored in the water pits), they are compromised and probably should not be used.
- Cross contamination of samples during processing is always a possibility and great care needs to be made to avoid this phenomenon. Samples are most vulnerable when in solution (i.e. the dissolution stage) where a process such as boiling samples on the same hot plate can facilitate cross contamination between sample solutions.
- Sub-sampling and dilution of the original parent solution is required due to the number of species to be measured from a single parent solution and the fact that many of the analytical techniques require minute amounts of samples. Sub-sampling and dilution has inherent errors such as operator errors, improperly calibrated scales and pipettes, contaminated equipment, etc. Sub-sampling can be accomplished by weighing or volumetric methods. Many scientists feel that the weighing method is more accurate and less problematic than volumetric methods.

[e] Section numbers provided in Roman numerals refer to the main body of this document.
[f] A good practice to follow is to label everything including the lids of the sample container.

- The sample's physical form is an important factor in handling. For example, solutions are easier to compromise: they can be spilled, are typically easier to contaminate, and can become unstable and key analytes may drop out of solution. The solvents may be corrosive and react with the vessel walls leaching unwanted materials out of the surface and/or compromising the container's integrity[g]. For this reason, solutions are often evaporated in a sample vial and then a solvent is added to the sample vial to bring the sample back into solution prior to use. This procedure has its own complication because everything doesn't always re-dissolve.

b. Reference materials and control standards

Section VIII reviewed reference materials and provided background on calibration, control and internal standards. This section provides additional information on reference materials.

- Make certain that the subcontractor lists all employed reference materials and copies of their "pedigrees" (i.e. NIST certificates). Note that reference materials can be concentration standards (provides a quantitative determination of the element in the standard), isotopic standards (provides weight percents for each isotope in the standard), and/or both.
- Beware of the pedigree of the reference standard. For example, one subcontractor used a ^{95}Tc tracer in the determination of ^{99}Tc in an unknown solution. After the analysis of half a dozen samples, it was found that there was a problem with the ^{95}Tc tracer: it contained ^{99}Tc to a significant degree. The ^{99}Tc "contaminant" in the tracer was present in a similar quantity as the quantity of ^{99}Tc in the unknown solution. The result could be corrected by back-calculating out the amount of ^{99}Tc in the tracer, but this correction introduces a large uncertainty in the final answer and an alternate analysis method needed to be developed and successfully executed.
- The subcontractor needs to properly maintain the reference materials to avoid contamination of the standard, ensure that it is not diluted or concentrated, etc. Reference materials need to be checked periodically to ensure their integrity is maintained.
- Sometimes inappropriate standards are employed for the application. This occurs when the subcontractor does not have the proper standard and tries to "make do" with what they have. This can have a negative impact on the data. For example, if the isotopic composition of the samples to be analyzed is 0.5 weight percent ^{238}U, using a standard of 20 weight percent ^{238}U may be inappropriate.
- How the reference standard is weighed (or aliquoted) out for addition to the sample solution is very important.
- Sometimes there is no available NIST standard for an element to be analyzed. In these cases, the subcontractor may use a high purity reagent, analyze this prepared standard as carefully as possible and employ multiple analysis methods if available. In this way they characterized their own standard. This type of standard is a secondary standard that is being employed as a primary standard. This is not a perfect solution, but the only viable one in such an instance. In the future it would be beneficial to compare these "home-grown" standards between laboratories that have their own in-house fabricated standards for the same element.

[g] Samples were stored at one facility in polyvinyl chloride containers that actually disintegrated after a couple years of storage due to both the nitric acid solvent and high levels of radioactivity.

Table D-1 provides a summary of definitions for the different reference material types. Table D-2 summarizes the different flavors of reference material types and how they are used.

Table D-1: Reference Material Definitions

Type	Definition
Reference material	A material or substance that has one or more properties that are sufficiently well established to be used for the calibration of equipment, the assessment of a measurement method, or for the assignment of values to materials.
Standard reference material	A reference material distributed by a number of vendors that has been certified either by direct or indirect comparison to a known standard typically provided by the National Institute of Standards and Technology (NIST).
Primary standard	A substance that has an accepted value (within specific limits) and is used to establish the value of the same or related property of another material. Note that a primary standard for one purpose may have been a secondary standard for another.
Secondary standard	A standard whose value is based upon a comparison with a primary standard. Note that a secondary standard for one purpose may have been a primary standard for another.
Internal standard	A standard that is deliberately added to the analyzed unknown sample to aid in the quantification process. These standards are used for the internal standard technique which is based on comparison of the signal corresponding to the analyte to be quantified with that of a reference called the internal standard. This technique allows the elimination of various error sources other than the intrinsic error due to counting statistics. These standards are typically added early on in the radiochemical processing and are usually chosen with chemical and physical properties as close as possible to the properties of the analyte. The internal standard will undergo the same loss during the radiochemical processing steps eliminating the need to determine an exact chemical yield (and eliminates the uncertainty associated with determination of exact chemical yield).
External standard	A standard containing a known concentration and volume of the species of interest which is analyzed separately from the unknown sample under identical conditions.

Table D-2: Standard Summary and Usage

Type	Typical Use
Calibration standard	These standards are primarily used as an external standard to calibrate instrumentation for analytical measurements and are often used as references for control charts. The standards will typically be selected to cover the range of analyte(s) to be measured. For example, the calibration standard used to calculate the energy calibration curve for a gamma ray spectrometer will be composed of the isotopes that cover the entire energy range that will be measured. These standards correct instrumental characteristics but provide no check of the chemistry. Note that these standards are typically primary standards but some laboratories use in-house secondary standards.
Check standard	A standard used for physical calibration and is measured periodically. The results are typically plotted on a control chart to evaluate the measurement process. A check standard may have been used for calibration, but if used as a check standard it is generally not considered to be useful as a primary calibration standard since it is used so often. The more standards are handled, the more likely it is that some change may occur which would affect the standard. Small changes that would still leave a process under control might not be suitable as a primary calibration standard. The more things are handled, the more uncertainty there is likely to be as to the actual standard value.
Control standard	A material of known composition that is analyzed concurrently with test samples to evaluate a measurement process. These external standards are usually fabricated in-house. They will match the characteristics of the samples to be analyzed as closely as possible, be analyzed using the same method to be employed for the samples to be analyzed, and are characterized using calibration standard(s) and frequently are tracked on control charts. These customized controls are very useful since it is rare to find a NIST standard with the same characteristics as a real world sample. Such standards are defined as "secondary standards" since they are calibrated against primary standards. For example, if the uranium isotopic abundances of the analyzed samples fall outside of the available NIST uranium isotopic standards, a suite of controls are created that cover the range of expected uranium isotopic abundances of the samples to be analyzed. These standards typically provide an instrumental check. However, they are sometimes used to check the chemistry by processing the "controls" via the same process as the samples being analyzed: such a procedure provides a check for both the chemistry and the instrument. Note that the term "control standard" is used by some laboratories to refer to reference or "blind" quality control standards.
Spike	A special type of an internal standard which is typically used in the method of isotope dilution mass spectrometry (IDMS). This method is based on the determination of the isotopic composition of an element in a mixture of a known quantity of an internal standard (which is called a "spike") with an unknown quantity of the element to be measured. The spike is a solution containing a precisely known concentration of the particular element to be analyzed whose isotopic composition has been changed by enrichment of one of its isotopes. The sample to be analyzed contains an unknown concentration of the element whose isotopic composition is unknown. When a known amount of the sample solution is mixed with a known amount of spike, the isotopic composition of the mixture can be used to calculate the amount of the element in the sample solution. Isotope dilution analysis can be used for all chemical elements that have two or more isotopes (provided that a well characterized enriched spike is available).

Type	Typical Use
Tracer	A type of internal standard which is a radioactive substance added to an experiment usually to trace (with a Geiger counter or similar equipment) the movement of the non-radioactive component of that element through the experiment. Also a tracer can be a known amount of an enriched stable isotope added to an experiment usually to determine the amount of the non-tracer component of that element using a mass spectrometer. In this case the tracer is also referred to as a spike (see discussion under "spike" above).
Cold reference	These references are unirradiated samples of the physics irradiation test program specimens that were irradiated and are used to provide the pre-irradiation compositions for comparison to the measured end-of-life data. These references are key in determining the build-up or loss of any given species through the irradiation process.

Section VI outlined the difficulty in having a good over all control sample(s) for the physics irradiation test program experiments due to the complexities of the sample. Thus, most of the controls used in the experiments were "partial" controls that just track one aspect of the experiment. For example, mass spectrometric controls to establish operating characteristics of the equipment. In this case it is important that the selection of controls bracket the range of isotopes that will be measured.

There are important questions to ask the subcontractor about their controls: what are their standard controls in their quality assurance program and do these controls work for physics irradiation test program samples, or are the compositions so different they are useless?

c. Blanks

It is important that the test sponsor understand the blanks that are run with the samples and that they are sufficient to track all possible contamination that may occur during the experiment. The test sponsor should consider the following points.

- There a number of common oversights that can be made with blanks. Examples: the blank does not contain all reagents, the blank does not go through all the same processes as the sample, or the blank is not processed in parallel with the sample.
- What else does the subcontractor analyze and how well do they perform the analyses? The answer to these questions can aid the test sponsor's assessment of the subcontractor's quality control. For example, if their thermal ionization mass spectrometer (TIMS) is used to measure environmental samples AND high level samples, laboratory practices have to be fastidious enough to maintain a "clean" mass spectrometer, or else the environmental samples will be compromised. They will probably have higher cleanliness standards than a laboratory that processes high level samples alone.
- What type of samples was processed prior to the program samples and was the hot cell or laboratory hood cleaned prior to processing the program samples? For example, what did the laboratory process prior to physics irradiation test program samples? If the processed samples contained high plutonium concentrations, then be mindful of a higher potential for plutonium contamination (since physics irradiation test program samples don't have much plutonium in

them and are more susceptible to contamination from plutonium in the processing environment).

- The test sponsor should be aware of the laboratory's cleaning practices and how they monitor their cleanliness. The laboratory should employ high purity reagents and all labware should be properly cleaned and kept clean. Laboratory dust may contain calcium, silicon, aluminum, iron, sodium, magnesium, uranium, titanium, copper, and manganese, as well as other elements.
- The test sponsor should know the inter-laboratory and extra-laboratory quality assurance programs that the subcontractor is involved in and how well they performed these programs.
- Insidious changes can affect analysis. For example, if a manufacturer out-sources production of a chemical, perhaps the change doesn't affect other analyses, but they can have a significant effect on the analysis for a particular sample type. An example of a seemingly insignificant change resulting in bad data is as follows. A series of rare earth elements were determined using neutron activation: the samples were sealed in a quartz container and irradiated in a test reactor. There was a problem with chromium contamination of a series of these samples. The laboratory re-traced their steps to find the source of the contamination so that it could be corrected. Reagents, equipment (special tools were electroplated with high purity gold before handling the samples to prevent contamination), sample containers, every facet of the experiment was checked for contamination. The problem was finally traced to the torch tip used to seal the quartz container. The over 20 year old torch tip had been replaced with a new one which had not yet completely out-gassed contaminating the sample vial and thus the samples.

Blank correction is performed by subtracting the contribution due to the blank from the measurement for the sample. It is important that the measurements for the blank and sample represent the same physical quantity. For example, if the blank results are provided as grams per gram of parent solution and the data are reported as grams per test specimen. The blank needs to be converted to grams per test specimen prior to correcting the test specimen's data.

Many subcontractors will not background correct the reported data since typically there is no significant background (analyte in the blank is 1/1000 of that in the test specimen). The test specification should specify that the subcontractor document their blank corrections including the blank type, how it was processed, the results and whether or not the data were blank corrected.

Sometimes measurements are made to verify that a sample does not contain a given analyte or that the analyte is present in quantities very close to the typical laboratory background. The subcontractor is effectively measuring "zero[h]" analyte. In these cases, a blank correction can result in a negative number for the analysis. A very small negative number is not unusual in such cases because the number is actually zero. Statistically the data population will be distributed around zero with positive and negative values with an average of zero. It is incorrect to "round" negative numbers to zero – this skews the average.

[h] Very often "zero" is not absolute zero quantity, but the detection limit of the instrument (the instrument's "effective" zero). Refer to the next section on detection limit.

d. Detection limits

The detection limit is simply defined as the smallest concentration/amount of the species of interest that can be measured by a single measurement with a stated level of confidence. However, the issue is complicated by several different detection limit types which are often instrument and/or administratively dependent.

- Minimum Detection Limit (MDL) is the lowest instrument response above zero detectable that is readable by an instrument and at least two times the amplitude of the noise.
- Limit of Detection (LLD) for counting data is the square root of two times the background and multiplied by 3.29. This definition describes a 95% confidence interval on a two-sided normal distribution.
- Minimum Detectable Activity (MDA) for counting data is the square root of two times the background and multiplied by 1.645. This definition describes a one-sided distribution.

It is important to carefully define how a detection limit is calculated since it affects how the data may be applied.

e. Internal versus external precision

Internal and external precision are terms that are sometimes employed by certain instrumental techniques and are defined here to avoid reader confusion when encountering these terms. Typically these terms are used in TIMS analysis and the term "internal precision" is actually a misnomer. In this context, the internal precision is defined as the precision for a single measurement. Since there is no such thing as a precision for a single measurement, this term is defined as the counting error for a single sample analysis. External precision refers to the standard deviation of multiple measurements of the same sample solution. For example, in TIMS measurements, the internal precision refers to the counting error for an analysis of one loaded filament. To determine the external precision, a portion of the sample solution is loaded onto multiple filaments and the reported value will be the mean of multiple measurements: the precision is the calculated standard deviation of that mean. The "external" precision is almost always larger than the "internal" precision since the external precision is dictated by a larger number of parameters such as filament to filament variation and differences in sample loading. Internal precision for counting techniques is primarily dictated by counting statistics although there are other factors that can affect it. External precision is a better estimate of the error of the overall measurement process since the precision of the instrumental measurement is affected by the sum of all instrumental measurement parameters.

8. Dissolution Process

For successful quantitative analysis, the samples need to be completely dissolved, be homogeneous, in equilibrium with the spike (if added), and all atoms of the element in the same oxidation state. Everything needs to stay in solution until they are no longer needed to be in solution (when the samples are run through separation and purification processes). The following points provide some pitfalls in this tricky process. Note that these processes are analyte concentration dependent and are affected by other species in the solution and their respective concentrations.

a. Pitfalls common to all dissolution methods:

- Precipitation is a major problem in quantitative analysis (unless the precipitation happens after the sample is spiked). This process can occur at any point in the analysis. Sometimes, the precipitate can be re-dissolved. Oftentimes dissolution is very difficult and/or the addition of additional chemicals can cause other problems in the solution (i.e. cause a different precipitation to occur). Also keep in mind that absence of a visible precipitate is not positive proof that precipitation has not occurred due to the very small amount of many of the analytes that would not be visual to the naked eye (especially looking through the sample container and the 3-foot thick hot cell window).
- Some test sponsors will not consider a precipitate of a non-analyzed constituent (i.e. a major constituent element that is not being measured) as being a potential source of error. However, if a large amount of precipitate of one element is falling out of solution, it can carry other elements out of solution with it. This is referred to as co-precipitation. This phenomenon has been observed in the processing of program samples and can result in the loss of elements such as cesium or cerium. Co-precipitate is not always a problem in that this process is constructively used in some analytical processes. For example, co-precipitation can be used to carry an element of interest on a different element for carrier free separations. Co-precipitation as a deliberate process is not a problem. Uncontrolled co-precipitation is typically undesirable.
- Plutonium is famous for polymerizing in a solution. It happens in dilute nitric acid solution (~0.1 molar solution) and typically occurs after an induction period. The rate is thought to be third order with plutonium concentration. Once the polymer has formed, it is next to impossible to dissolve. Some success has been obtained by wet-ashing the samples with concentrated nitric acid, and re-dissolving in concentrated nitric acid. The concentrated nitric acid inhibits the production of the plutonium polymer. It is also known that uranium can induce plutonium polymer formation by combining with nitrate ions in solution and thereby reducing the nitric acid molarity.
- Constituents can also adsorb onto the sides of any sample container (or on dust/particulates). Since some elements are present in very low concentrations, the atoms can attach themselves to active sites on the container's surface. This is truer of glass than plastic and is also more likely when the solution is closer to neutral. It is also possible for a radioactive species from the sample to exchange with a chemically stable atom of the same element that is part of the container composition.
- Some radioactive species combine with solvents such as oxalic acid to form oxalate complexes. For example, uranium combines with oxalate to form a soluble complex that chemically behaves differently than the uranium ion would. It may be more stable in the complex form and thus not be separated from other elements as expected. Other organic compounds such as Ethylene diamine tetra-acetic acid (EDTA) can do similar things. In addition, there are complexes formed with non-ionic species such as water or ammonia which also can change the behavior of the ion in solution.
- There is a problem with very dilute solutions and carrier free chemistry. Going to a 1,000,000th dilution for species that are present at the level of 10^{10} atoms is very tricky. Since the number of atoms is "small," the loss of a small number of atoms can make a large difference in the result. An example of this would be a ^{137}Cs ion in solution can exchange with stable cesium (or

potassium) present in the structure of the container. Since the container ions are stable, they would not be detected by gamma spectroscopy and the lost ^{137}Cs would not be known. A solution to this problem is to add a holdback carrier to the solution. Such a carrier might have 1.0 mg/ml of cesium in it. This would be ~ 5 x 10^{18} cesium ions so that any exchanges that take place with the container would be primarily stable cesium and would not affect the ^{137}Cs results.

- Ruthenium can be lost by volatilization, as well as by precipitation. Black precipitates containing ruthenium have been detected in the past. At the time they were thought to be uranium ruthenide, however it is more likely that this was ruthenium dioxide, which forms a black precipitate. The volatile compound is probably ruthenium tetra-oxide which boils at 100^{o}C. This compound can be lost during dissolution and care should be taken to avoid its generation.
- Major components in the sample can form an oxide. When this oxide drops out, uranium and other elements of interest can be carried with it due to the flocculent nature of the precipitate. It is soluble in concentrated HF, but this causes the other problems that are associated with excess fluoride. The excess fluoride can be complexed with boric acid but there are no guarantees that the insoluble fluorides have not already precipitated.
- If iron is present in a basic solution, iron hydroxide can form. Iron hydroxide is a great scavenger and can cause problems in the downstream separation chemistry since it can carry other ions with it. In addition, basic chemistry can cause many insoluble hydroxides to form and confound the analysis. Iron can be retained on the same cation exchange column as uranium. This can impact the efficiency of the uranium separation in those cases where iron is more readily adsorbed since excess iron will use up the column active sites and allow the uranium to pass through.
- Other insoluble fluorides can be generated by other materials present in the sample. This is why it is imperative that the radiochemists are provided approximate concentrations that may be present in the sample.

b. Pitfalls common to sulfate fusion dissolution:

For the sulfate fusion method, the sample is put in a quartz beaker with approximately 50 grams of potassium or sodium pyrosulfate ($Na_2S_2O_7$) and then heated to 1000^{o}C in a Hoskins furnace. The resulting fused solid is dissolved in nitric acid. Oxalic acid (HO_2CCO_2H) is then added to complex the uranium (in the U^{+6} valence state). The following points provide additional issues with this type of dissolution process.

- Some major components can form an oxide which can be seen in the solution as a white powder. The way to dissolve this oxide is to add HF. However, as already discussed, additional HF can cause fluoride precipitation.
- After dissolution, the oxalate needs to be removed from the solution since oxalate can interfere with downstream chemistry. Oxalate removal can be accomplished by wet-ashing with nitric acid. This process results in salts remaining in the bottom of the sample container which then can be brought up in a solvent dependent upon the extraction chemistry to be used.

- The wet-ash method also works well to get rid of Pu polymers and complexes. Plutonium chemistry is nasty. Plutonium does weird things in concentrated nitric acid. Plutonium likes to form a polymer and also likes to adsorb onto the walls of the container when in weak acid solutions. Plutonium readily exists in a solution in multiple valence states. Plutonium can be placed in equilibrium by treatment with iodic acid (HIO_3) to run up the valence to +6 for all the plutonium in the solution. Then depending on the desired valence state, the valence state can be reduced to +3 or +4. One method to perform this reduction is to use hydroxylamine.

c. Pitfalls common to nitric acid dissolution:

In the nitric acid dissolution, the sample is placed in nitric acid and is heated either on a hot plate or in a microwave. As previously discussed, without the addition of hydrofluoric acid, complete dissolution will not occur. This is the same chemistry that was employed in the recovery program where any precipitation of highly radioactive species could be disastrous. In the large scale chemistry, the dissolver solution was at a higher volume than for these small bench top samples. The hydrofluoric acid addition could be precisely controlled and concentration could be monitored very carefully. This control and monitoring ability for a plant scale process is impossible to duplicate in a test tube on the bench top! The following points pertain to this type of dissolution.

- When too much hydrofluoric acid is added, fluoride precipitation occurs. This precipitation is nearly impossible to get back into solution.
- Boric acid is used to complex the excess fluoride to prevent fluoride precipitation. This process requires a really good chemist or chemical technician to watch the process. It doesn't take much inattention to add too much HF.
- The addition of boric acid and/or EDTA can cause its own set of problems with complexing some of the fission products.
- There is an increased chance of the plutonium polymerizing the longer the dissolved solution is left in nitric acid.

9. Radiochemical Separation and Purification Techniques

Section VI provided background for radiochemical separation and purification processes. In this appendix, some details for some of the methods will be discussed in the sample preparation section for each method. Documentation of all possible methods for separation and purification of every analyte is beyond the scope of this document. However, this appendix will capture the idiosyncrasies of the various methods employed for physics irradiation test program samples. Since radiochemical separation and purification techniques are typically driven by the measurement technique, details will be found in sections detailing each instrumental technique.

Note that because many of the analyses are done without the addition of any carriers, there are many methods whereby errors in recovery can be introduced into the system. These errors include carrying of trace elements along with the precipitate of a different element and precipitating an element without realizing that you have exceeded the solubility product of an element.

10. Radiochemical Carrier Chemistry

There were several references to "carriers" in Sections III, VI and X. However, there was no explanation of carrier since radiochemical carrier chemistry is not extensively employed for the physics irradiation test program samples. Providing additional definitions to an already confusing array of chemistry terms would not have been of much benefit to the reader at that point in the document. However, it is beneficial for the reader to have a basic understanding of radiochemical carriers when examining some of the more detailed references on the employed experimental methods.

Much of radiochemistry involves the handling of extremely small traces of elements or compounds through dilution, chemical separation, and purification processes. Some separation methods work well at low concentrations while others are less effective.

The typical object of carrier chemistry is to isolate the trace analyte with a known (hopefully high) yield in a form which is chemically and physically stable. It is typically required to add a weighable quantity of carrier to help recover the trace analyte and sometimes required to add carriers for other elements (that often are present in much higher concentrations than the trace analyte) which must be excluded. Barium can be added to fission product solutions when performing a strontium separation. Strontium nitrate is insoluble in nitric acid while barium nitrate is not. If the barium was not added to the solution, the beta emitting barium isotopes could co-precipitate with the strontium nitrate and give an excessive count rate when doing the strontium beta counting. This is a good example of the use of a holdback carrier.

Table D-3 summarizes the most common carrier types. Note that this is not an inclusive list of carrier types and it is also not unusual for chemists in different disciplines to use different definitions (e.g. biochemistry verses radiochemistry). One classic use of a carrier is use of one element (e.g. barium) to precipitate something else (e.g. chromium) out of solution to provide a weighable sample. A term for this carrier type cannot be found in the table since it does not have a designated name. Another usage is where a cation, such as palladium, is added to precipitate an anion, such as iodine (as the iodide) or vice versa if the palladium was of interest. All examples in the table are of the same charge.

Table D-3: Carrier Types[i]

Type	Definition	Primary Use	Example(s)	Notes
Isotopic	The added carrier differs only in isotopic composition from the trace element that it needs to carry	Quantitative determination of a trace amount of a radioactive nuclide	Additional of a known amount of Ba^{++} (i.e. 10 mg of barium chloride or nitrate) to ^{140}Ba (the trace isotope to be measured) and then precipitate the barium as carbonate. The final precipitate (in principle) can be weighed to determine the extent of the recovery of the radioactive barium.	Important criteria that needs to be met: • the carrier quantity must be accurately known & large when compared with that of the trace element • the carrier must be added as early as possible in the chemical procedure (i.e. typically immediately after dissolution to the aliquot being analyzed), typically in an acid solution, to avoid extraneous reactions that might separate the trace element radioactive isotope and the carrier • physical & chemical mixing must

[i] Reference: Donald R. Wiles, "Chemist-at-Large" at Carleton University: http://http-server.carleton.ca/~dwiles/CRNL/section_four.htm

Type	Definition	Primary Use	Example(s)	Notes
Isotopic *continued*				be complete: undissolved particles, colloids, etc. need to be considered – chemical mixing is particularly important where exchange among different forms may be slow • the carrier and sample must be in the same ionic state (i.e. all +3) and may need to perform multiple reduction/oxidation steps to insure this is achieved
Iso-morphous	A carrier whose chemical properties (typically valence shell electron configuration, oxidations states, ionic radii, solubility of pertinent compounds) are essentially identical to those of the trace element to be measured. May have characteristics that allow separation of the carrier from the trace element to be measured at the end of the process if necessary for downstream analysis.	Typically added to prevent loss by adsorption	Use of barium as a carrier for radium, lanthanum for promethium, rhenium for technetium, etc. Example of a carrier that can be eventually separated from the trace element to be measured: cerium as a carrier for the lanthanides, cerium can be oxidized and its chemistry no longer resembles that of the other lanthanides.	An added bonus: • Particularly useful if either the carrier or the trace element to be measured exists in an additional oxidation state: then there is a possibility of removing the carrier at the end of the analysis, leaving the trace element to be measured essentially carrier free. This is desirable if the carrier would interfere with downstream analysis.
Pseudo-morphous	A carrier which is not strictly isomorphous with the trace element to be measured but in certain attributes is closely analogous to the trace element to be measured. These carriers typically form anomalous mixed crystals with the trace element to be measured. Goldschmidt's laws[j] generally apply to these situations.	Typically added to prevent loss by adsorption	Pb^{++} can be used as a carrier for Ba^{++} when the salt is precipitated as the carbonate or sulfate. If the carrier needs to be removed, the Pb can be removed as the sulfide by carefully avoiding oxidizing agents. Lanthanum at low concentrations (0.1 mg/ml) can be used to carry plutonium as the fluoride if electroplating is undesirable.	These two precautions should be considered: • The insoluble salt formed by the tracer element should not be more soluble than the comparable salt of the carrier; otherwise the tracer element will tend to concentrate in the solution. • The precipitation must be essentially complete in order that the weight of the recovered carrier represents the trace element recovery. As long as the fractional recovery is known, the physical recovery of the precipitate is less important.
Scavenger	A carrier added to a solution to carry or remove several elements in order to remove them for subsequent more selective chemistry or to prevent them from interfering in later steps.	Addition to a mixture to remove impurities that would interfere with down stream processing and/or analysis	The carrying of many elements on ferric hydroxide (a high surface area precipitate). Barium sulfate precipitate can be used to carry thorium and the transuranic elements without carrying uranium. This is a nice way to measure gross alpha without uranium.	Works best when: • precipitate has a large surface area • the trace element itself forms an insoluble compound under the same conditions • the opposite charge ion is present in excess

[j] Any cation is acceptable in the lattice of another compound if the oxidation states differ by no more than 1 and that the ionic radii are different by no more than 15%.

Type	Definition	Primary Use	Example(s)	Notes
Holdback	A carrier added to prevent a particular species from following another species in a chemical or physical process. This carrier is chemically the same or very similar to the trace element.	Prevent losses by adsorption	Stable cesium carrier is added to a solution to prevent the loss of ^{137}Cs by adsorption on the sides of a container.	Caution: • The holdback carrier needs to be added before the possibility of loss of the species of interest.

In addition to the carriers described in Table D-3, there are also a number of unclassified carriers. These carriers work, although without making any obvious sense and cannot be explained by simple theories or in some case even goes against established rules. For example, barium sulfate can be a good carrier for thorium provided sufficient potassium is present. Another example is that manganese dioxide is a strong carrier for radium, for no obvious reason.

Keep in mind that carrier chemistry can be more of an art than a science and there are no hard and fast rules. However, it is generally observed that conditions which favor precipitation of large quantities of a radionuclide will also favor precipitation of the trace element quantities in the presence of the appropriate carrier.

11. Instrumental Analysis Techniques

Most instrumental techniques share common elements that can be divided into categories. This section will summarize attributes employed in the following sections that provide information that is common to the majority of analytical instrumental techniques. Following this section, in-depth discussions for each category (where pertinent) will be provided for each instrumental technique. Please note that this discussion is not all inclusive and only provides the information provided by the subcontractor or from the author's experience for the processing of physics irradiation test program samples.

a. Sample preparation

Every instrumental technique requires the specimen to be in a proper form for analysis. These preparations can be as simple as ICPMS sample preparation where the sample is diluted to the proper concentration and then loaded into the instrument (referred to as "dilute and shoot"); or the preparation can be as involved as IDMS techniques where unspiked and spiked samples need to be performed for each measurement and the element of interest requires complete separation from all other constituents.

In the following sections for each technique, sample preparation will be divided into three categories: 1) sample processing (separation and purification) of the element(s) to be analyzed; 2) sample loading of the separated and purified sample into the instrument; and 3) chemistry idiosyncrasies related to sample preparation. The information will be organized by instrumental technique with details provided for individually measured elements. For techniques where more than one analyte is measured simultaneously, the information will be provided on the group of analytes, providing information on any individual analyte which requires special processing.

b. Quality control

Every analytical laboratory has a routine quality assurance program to ensure that the instrument is functioning within normal operating limits. A good laboratory will thoroughly check out the instrumentation prior to the start of a new experiment and will also periodically check the instrument's operating parameters during the analysis of the sample set. The frequency of this check is dependent on the instrument and the type of analysis being performed.

- *Calibration*: Every analytical instrument employed for quantitative analysis requires some type of calibration. The initial calibration may be complicated and even performed by the manufacturer. The calibration should be periodically checked, typically by measuring a check standard, to ensure that the instrument remains in calibration. Note that for some instruments, individual components may require independent calibration. For example, in multiple collector TIMS instruments, the efficiency of each Faraday cup is independently measured, then a control standard is used to check the response of the integrated unit as a whole.
- *Control charts:* Control charts are used to establish if control specimen results fall within the limits which define the range of expected values when the system is in a state of statistical control and thus functioning properly. Oftentimes if the values do not fall within the limits, there is a problem with the instrumentation which needs to be corrected. However, note that the problem can also lie in a problem with the control specimen itself or in the preparation of the control specimen prior to analysis. Typically, if the processed specimen is out of the control values, one assumes the process is problematic, not the instrument. At this point the whole set needs to be repeated at the point where it is identified that the process went "bad". One assumes the instrument is the problem when the control specimen is not processed and is loaded directly into the instrument (i.e. TIMS analysis of NIST standards).
- *Instrument log books*: Instrument logs track the key operations of the instrument, dates when maintenance is performed and what was done, any changes made on the instrument (this includes software changes[k]), any problems with the equipment or samples, any observations, etc. Such logs are indispensable in trouble-shooting issues that may reveal themselves downstream of the analysis. Sometimes systematic errors in the data can be remedied by looking at the instrument logs and controls charts. The information in these sources can provide data to enable quantification of the experimental bias enabling correction of the data.
- *Maintenance*: Routine maintenance is an often overlooked component of maintaining quality control of an instrumental technique because potential problems caused by wear or build-up of foreign material can be avoided. Analytical instruments employed for quantitative analysis are typically very complex and highly automated. Routine maintenance is the key to ensuring the peak performance of these complex instruments. In some laboratories, scheduling demands provide pressure for sample throughput at the expense of routine maintenance. This philosophy may adversely impact data quality and may also result in extended instrument downtime resulting from inadequate upkeep of the instrument. The experience is that routine maintenance at regular time intervals (and/or after a certain number of processed samples) maintains the integrity of the instrument and the analyses and also reduces the down-time due to malfunctions. A well-maintained instrument is imperative for high quality, accurate, quantitative analysis.

[k] This helps in future trouble-shooting processes, since some problems are not hardware problems, but are related to the software and/or the interfaces.

c. Instrumental analysis

Each technique has a standard sequence of steps to accomplish an analysis for a given sample type. For a given technique, it is important to perform each analysis as closely as possible for each sample of the sample set to provide consistency. Deviations from this occur for "special" samples such as samples that contain very low analyte concentrations (and thus provide very low signals). A well designed experiment will provide accurate results over the entire concentration range of the sample set without significant deviations in the experimental methodology. The following sections on the individual techniques will provide a general method for each instrumental analysis and instrument specific considerations.

d. Data reduction

All data need some level of data reduction. Data reduction is technique dependent and also relies on the complete methodology and desired quantity. For example, different calculations are performed if the answer is to be reported as a concentration, or as a total analyte amount for the original sample. Some instrumental analyses require more "corrections" to be applied to the data. It is important for the test sponsor to know how the data were calculated and exactly what quantity is being provided. If there is a problem with the data, it could be a simple calculation error where a decay correction was made improperly, instrumental biases were not corrected for, background was not subtracted, the result was reported with the wrong units (i.e. weight percent instead of atom percent), etc. Oftentimes it is difficult to get the appropriate information to determine the exact calculation method. Much of the data reduction software is now provided by the manufacturer (oftentimes with default values that need to be changed by the user[1]), and it is sometimes difficult to determine exactly how raw data are processed.

Information on basic data reduction including corrections that may need to be made (i.e. background correction) will be provided (if available/applicable) for each individual technique in the following sections.

e. Instrumental "quirks"

Each type of instrumental analysis has its own "quirks" that are known by experienced analysts. These are points that are valuable to keep in mind while examining preliminary data from a subcontracting laboratory. Some of the instrumental "quirks" are analyte dependent. Any known instrumental "quirks" that can affect the analytical results will be provided for each individual technique in the following sections. Note that this information is not inclusive of all possible instrumental "quirks" that may occur.

f. "Rules-of-thumb" and "common-sense-checks"

An experienced analyst will be aware of information which is commonly referred to as "rule-of-thumb" that provides insight on what to expect from an analysis. For example, in mass spectrometry the accuracy for a measured weight percent directly correlates with the isotopic abundance of the isotope being measured. Analysts will frequently know other information that can shed light on their analyses. For example, the amount of uranium depletion provides information that is useful for the scientist measuring fission products from the same sample solution. The amount of fission product will correlate with uranium depletion: the more depleted the sample, the

[1] Sometimes the software will revert back to the default values and this fact may not be discovered by the analyst for quite some time.

more fission product should be present (unless it has decayed away). This is common sense. If the largest amount of fission product is measured for the sample that is the least depleted, there is a potential problem with the fission product analysis, or the uranium analysis is in error. Either way, the result is a flag that the data set is not passing the "common-sense" test. This type of information will be provided (if available/applicable) for each individual technique in the following sections. Note that this information is not inclusive of all existing "rules-of-thumb" and "common-sense" for any given technique.

g. Trouble-shooting and recovery methods

An experienced analyst will know tricks of the trade to trouble-shoot their instrument when it is operating improperly and/or ways of recovering data when the analysis goes "bad" for one reason or another. Mass spectrometrists will often calculate atom rates with different reference isotopes to determine if there is an isobaric interference or monitor a mass unique to a known isobaric interference. This type of information will be provided (if available/applicable) for each individual technique in the following sections. Note that this information is not inclusive of all existing trouble-shooting and recovery methods available for any given technique.

h. Identification of common experimental problems

Table 5 on page 53 provided a summary of some experimental problems that are common to almost all experimental techniques. This appendix will provide a summary of some common experimental problems unique to each experimental technique. Note that this information is not inclusive of all possible instrumental problems that may occur.

The following sections will provide additional information on each analysis technique. The information is not all inclusive, but attempts to capture as many details as can be collected from knowledgeable experts prior to their departure from the program. Please note that this is not an attempt to chronicle exact procedures for the analysis of each analyte. Refer to the applicable references for those details.

The analyte that has been measured for program samples is listed under each technique. Some analytes can be measured by more than one technique and may occur in multiple sections. Analyses are not necessarily chemical element "dependent" because different techniques may be used for different isotopes of the same chemical element. Please note that the quantity of documentation for each technique differs as a function of the technique's complexity, number of known problems, information provided by the remaining program "experts", and how prevalent the technique was employed for analysis[m].

The reader should keep in mind that although this entire appendix is divided into segments for explanation purposes, the experiment needs to be examined as a single entity since all parts are interdependent. An error in the dissolution/dilution process can affect data reduction at the end of the experiment. A common trap is for the experimentalist/test sponsor to become too focused on one aspect of the analysis, missing an obvious error somewhere else in the methodology.

[m] For example, ICPAES was used only for the determination of a couple of chemical element totals.

12. Alpha Spectroscopy Technique

Section VII.B.1 provides background and references for this technique. This section provides additional details and program examples.

a. Analytes

Alpha spectroscopy has been used to measure ^{241}Am, ^{242}Cm, and ^{244}Cm for physics irradiation test program samples.

The method has also been used to measure ^{233,234,235,238}U, ^{238,239,240,242}Pu, and ^{228,232}Th for other types of program samples, particularly for environmental and radiological control samples.

b. Sample processing

Very often internal standards are employed. To illustrate the use of an internal standard, the uranium analysis of soil samples will be used as an example. A calibrated spike of ^{232}U is added prior to leaching the sample with acid. The sample is digested (heated over a period of time) and then uranium chemistry is performed using AG-1 resin which separates out both uranium and iron[n]. The uranium is removed from the column and electroplated on a platinum disk[o]. The sample is counted on an alpha spectrometer and the ~5.3 MeV peak from ^{232}U, the ~4.8 MeV peak from ^{233,234}U, the ~4.4 MeV peak from ^{235}U, and the ~4.2 MeV peak from ^{238}U are integrated. Since a known amount of ^{232}U was added, by ratioing the peak heights of the ^{232}U to the other uranium peaks (in this case $^{233/234}$U, ^{235}U and ^{238}U) the isotopic content can be determined. ^{233}U and ^{234}U are reported together because they have essentially the same alpha energy and are not resolvable. It is necessary to purify the ^{232}U spike periodically since the daughters grow in and don't always get separated from the uranium. Without this separation, several additional nuclides (^{228}Th, ^{224}Ra, ^{220}Rn etc.) present in the ^{232}U spike would potentially complicate the alpha spectrum. Similar methods are used for thorium using ^{230}Th as the tracer and for plutonium using ^{242}Pu as the tracer.

The internal standard accounts for the varying thickness which affects the resolution, but it assumes that the detector efficiency including sample thickness is constant with energy and thus there is no need to worry about the absolute detector efficiency. If the sample gets too thick, it isn't always a good assumption. This is why alpha spectroscopy is performed under vacuum. Also, tailing of high energy peaks into the lower energy ones can occur. If this effect gets too severe, the sample is redone.

c. Sample loading

The electroplated sample is placed under a semiconductor detector in a vacuum chamber. The chamber is evacuated and the counting is begun.

d. Chemistry "quirks"

Until the recent development of crown ether resins, it has been very difficult to separate americium from curium. These new resins have made it possible to perform the separation and then to

[n] Since soil contains a large amount iron, the column would be loaded mostly with iron and little if any uranium was kept on the column. This resulted in very low yields. Today UTEVA resin is available which doesn't remove iron allowing the column to absorb only uranium.
[o] Today chemists also use a NdF_2 precipitate which is an easier process.

determine the concentrations. It should also be noted that ^{243}Cm and ^{244}Cm have essentially the same alpha energies and cannot be easily separated using alpha spectrometry.

e. Quality control issues

The tracers described above serve as the internal standards.

f. Instrumental analysis

Key elements for successful alpha spectrometry are similar for other instrumental methods: good peak shapes, proper calibration, and low background. A sample that has too high a surface density will have poor peak shapes due to energy attenuation. If this happens peaks will have poor resolution and it will not be possible to separate the isotopes of interest.

g. Data reduction

Alpha peaks are integrated and if necessary corrected for abundance. The concentration of the spike is then ratioed to the isotopes of interest to determine the activity. If necessary the activity is converted to mass using the isotopic specific activity.

h. Instrumental "quirks"

Instrumental backgrounds need to be checked routinely since recoil products can end up depositing on the detector causing spurious counts that are added to the peaks of interest. If the background becomes too large the detector may have to be cleaned (if possible) or replaced.

i. "Rules-of-thumb" and "common-sense-checks"

The activity ratios of the various isotopes should be checked to ensure that there is no other element coming through the chemistry. If there is a suspicion that there could be something wrong, particularly with the isotope used as a tracer, an unspiked sample may need to be run. This is particularly true with thorium since ^{232}Th is a ^{238}U daughter and exists in natural thorium to varying degrees depending on the soil uranium content.

It is not unusual for alpha spectrometry to be combined with another method. For example, alpha spectrometry and TIMS is used for uranium analysis of environmental samples. TIMS is used to provide measurements for ^{233}U and ^{234}U (alpha can provide only a sum for these two isotopes due nearly identical alpha energies) and TIMS also determines if ^{232}U was present (this isotope is typically the added spike for alpha spectrometry).

j. Trouble-shooting and recovery methods

If peaks that are normally separated overlap, or the resolution of the detector appears to be worse than normal, there are several possible corrections. The sample may be too thick, necessitating reprocessing of the sample. The high voltage may be turned off or the vacuum chamber may leak. These are instrumental problems that can be easily fixed.

k. Identification of common experimental problems

Table 5 provided a summary of some experimental problems that are common to almost all experimental techniques and will not be repeated in this section. Table D-4 provides a summary of

common experimental problems that are unique to alpha spectroscopy. Note that this information is not inclusive of all possible experimental problems that may occur.

Table D-4: Summary of Common Alpha Spectroscopy Experimental Problems

Occurrence	Possible Cause(s)	Effect on Experimental Results	Possible Remedy
Check standard falls out of control chart acceptance band	• Change in instrumental operating characteristics since last calibration	• Results lower or higher than actual	• Recalibrate instrument
	• Instrumental problem affecting calibration	• Results lower or higher than actual	• Rerun calibration, trouble-shoot & repair as required
	• Compromised calibration standard	• Results lower or higher than actual	• Check calibration standard, replace if necessary
	• Improperly executed calibration	• Results lower or higher than actual	• Repeat calibration
Poor peak shapes	• Poor chemical separation of alpha emitter with nearly identical alpha energies	• Results higher than actual	• Repeat chemistry, revise procedure if necessary
	• Daughter build up in internal standard solution	• Results lower or higher than actual	• Process internal standard and remove daughters
	• Instrumental problem	• Results lower or higher than actual (e.g. if noise is added to a peak the results are higher than actual)	• Rerun calibration, trouble-shoot & repair as required
	• Energy attenuation due to too high sample surface density	• Results lower than actual	• Re-dissolve sample and reapply as a thinner layer
Poorly resolved peaks	• Sample too thick	• Results lower than actual	• Re-dissolve sample and reapply as a thinner layer
	• Leak in vacuum chamber	• Results lower than actual	• Fix the leak
	• High voltage turned off	• Results lower than actual	• Turn on high voltage
High background	• Recoil products deposited on detector	• Results higher than actual	• Clean, if does not remedy problem may need to replace components
	• Electrical Noise	• Results higher than actual	• Troubleshoot electronics

13. Beta Counting Technique

Section VII.B.2 provides background and references for this technique. This section provides additional details and examples.

a. Analytes

The beta counting technique has been used to measure ^{99}Tc and ^{147}Pm for physics irradiation test program samples.

b. Sample processing

A dissolved sample is processed to separate the beta emitter(s) of interest from other radioactive species. This can be done by passing the sample through a column or otherwise separating the element of interest by methods such as precipitation. In all cases, there will need to be some method for determining the chemical yield of the separation. This can be done by adding a known

quantity of the stable element used for precipitation and weighing the precipitate, or by adding a known quantity of a radioactive species of the same element that can be quantified by another counting method.

c. Sample loading

The separated sample is placed on a planchet, either as a sample weighed on filter paper or evaporated onto the planchet and weighed. The weight is necessary to calculate material surface density and thus the self-absorption correction as well as the chemical yield. The weighed sample is placed on a calibrated beta counting instrument to determine the activity present.

d. Chemistry "quirks"

Since there are no stable technetium isotopes, the chemical yield must be determined by another method. This means either co-precipitation with another element, typically rhenium, or by the addition of a known a quantity of ^{95m}Tc, which is a gamma emitter. The one potential problem with the latter method is the purity of the added tracer. If there is an unknown amount of ^{99}Tc present in the tracer, the actual chemical yield will be determined incorrectly.

^{147}Pm is another tricky analyte because this isotope has very little gamma emission; it is normally determined by beta counting. To do this, particularly for fission product mixtures, the promethium must be separated from the other rare earths, since many of them are also beta emitters. Since there are no stable promethium isotopes, ^{147}Pm is best obtained using a calibrated column. The ion exchange column must be calibrated such that each rare earth element elutes from the column in a different volumetric fraction. Then the promethium fraction can be removed, evaporated and counted. This calibration also includes knowing the chemical yield for the column fraction taken.

e. Quality control issues

It helps to have a gamma count of the ^{99}Tc separated material. This ensures that no gamma emitters such as ^{60}Co are carried with the ^{99}Tc.

Ion exchange columns don't always remain calibrated in the same way. Therefore it is useful to check the eluted volumes periodically to ensure that lower or higher atomic number rare earths are not being included in the promethium fraction.

f. Instrumental analysis

Most beta counting is done using a gas flow proportional counter. This instrument requires calibration for efficiency for each beta emitter of interest. It is also necessary to prepare self-absorption curves that allow the determination of efficiency as a function of sample weight. Since this is also a function of beta energy, it is often necessary to have self-absorption curves for several different isotopes. It is also necessary to ensure that the appropriate geometry is calibrated. A filter paper does not always take up the entire planchet and therefore the actual filter paper geometry will need to be calibrated.

g. Data reduction

Samples are counted and the counts per time unit (after background subtraction) are used with an efficiency factor to calculate the activity. Activity can be converted to mass if required by using the appropriate specific activities.

h. Instrumental "quirks"

Because proportional counter plateau can change, it is necessary to verify the plateau whenever gas bottles are changed. It is also necessary to monitor the background count rate as well as the efficiency of the instrument to ensure that it is operating properly. If evaporation is used to produce a sample for counting, the planchet should be evaluated for even dispersion of the sample. Sometimes the last residual liquid moves to the edge of the planchet. This can result in the sample being in a different geometry than was calibrated.

i. "Rules-of-thumb" and "common-sense-checks"

If count rates are unusually high, it may be due to the presence of other beta emitting isotopes. Checks can be made using the suggestion in the trouble shooting section below.

j. Trouble-shooting and recovery methods

If contamination of the sample with an undesired beta emitter is suspected, there are methods that can be used to help determine if this is true. One method is to gamma scan the sample to determine if any gamma emitters are present. One such case might be the presence of ^{60}Co in a ^{99}Tc sample. Another option is to perform a range-energy analysis[p] to determine if more than one beta energy is emitted by the sample. This would not work for the case of ^{60}Co and ^{99}Tc since they have similar beta energies, however, it can be used to determine ^{89}Sr in a ^{90}Sr sample. Another option might be to make use of a liquid scintillation counter with spectroscopic capabilities. However, this would probably require additional chemical preparation and instrument calibration.

k. Identification of common experimental problems

Table 5 provided a summary of some experimental problems that are common to almost all experimental techniques and will not be repeated in this section. Table D-5 provides a summary of common experimental problems unique to beta counting. Note that this information is not inclusive of all possible experimental problems that may occur.

Table D-5: Summary of Common Beta Counting Experimental Problems

Occurrence	Possible Cause(s)	Effect on Experimental Results	Possible Remedy
Check standard falls out of control chart acceptance band	• Change in instrumental operating characteristics since last calibration	• Results lower or higher than actual	• Recalibrate instrument
	• Instrumental problem affecting calibration	• Results lower or higher than actual	• Rerun calibration, trouble-shoot & repair as required
	• Compromised calibration standard	• Results lower or higher than actual	• Check calibration standard, replace if necessary
	• Improperly executed calibration	• Results lower or higher than actual	• Recalibrate instrument
	• Plateau change when gas bottle is changed	• Results lower or higher than actual	• Recalibrate instrument

[p] The range of a beta particle (mg/cm^2) is related to the beta energy and stopping material. See Reference 1.

Occurrence	Possible Cause(s)	Effect on Experimental Results	Possible Remedy
Incorrect efficiency correction	• Use of erroneous self-absorption curve (e.g. use of the wrong self-absorption curve for the measured nuclide)	• Results lower or higher than actual	• Use the correct one
Poor peak shapes	• Poor chemical separation of alpha emitter with nearly identical alpha energies	• Results higher than actual	• Repeat chemistry, revise procedure if necessary
	• Daughter build up in internal standard solution	• Results lower or higher than actual	• Process internal standard and remove daughters
	• Instrumental problem	• Results lower or higher than actual	• Rerun calibration, trouble-shoot & repair as required
	• Energy attenuation due to too high sample surface density (sample loading problem)	• Results lower than actual	• Re-dissolve sample and reapply as a thinner layer
Poorly resolved peaks	• Sample too thick	• Results lower than actual	• Re-dissolve sample and reapply as a thinner layer
High background	• Contaminated detector	• Results higher than actual	• De-contaminate detector
	• Electrical interference	• Results higher than actual	• Troubleshoot electronics

14. Gamma Spectroscopy Technique

Section VII.B.3 provides background for the technique. This section provides additional details and program examples. Counting was performed using an intrinsic germanium detector. It is possible to use other types of detector materials, but germanium detectors give the best combination of detector efficiency and resolution available today.

a. Analytes

The gamma counting technique was used to measure ^{134}Cs, ^{137}Cs, ^{144}Ce, ^{152}Eu, ^{154}Eu, ^{155}Eu for physics irradiation test program samples.

The method has also been used to measure uranium and thorium isotopes for past program radiological control and environmental samples, as well as used to monitor radioactivity during facility operations.

b. Sample processing

To obtain quantitative information from a gamma ray counting system the samples are placed into a counting geometry that the detector has been calibrated for efficiency. This is normally a flat geometry such as might be used for filter papers or as a known volume of liquid in a closed container. Each sample is placed in the known geometry and placed at a fixed distance from the detector. The sample is counted for a known length of time. It is not always necessary to separate an isotope of interest from other radioisotopes as is required for beta counting, since many isotopes have unique gamma ray decay processes that allow one isotope to be distinguished from another. It is also necessary to obtain a sample with a count rate that will allow the sample to be processed in a reasonable time. This requires the combination of gamma ray emission rate and distance from the detector to be adjusted to maximize the sample throughput.

c. Sample loading

Density of the sample must be measured. More dense materials can absorb weak gamma rays. Because gamma samples are often large in size, the actual material density may affect the counting efficiency. Therefore, it is either necessary to calibrate for materials of different densities or use a system such as Canberra's In-Situ Object Counting System. This system uses Monte Carlo models of a detector along with models of various materials to generate efficiency curves for various geometries and materials.

d. Chemistry "quirks"

Gamma spectroscopy is not sensitive to chemical form except for density. There can be cases where precipitates can form in liquid samples allowing some isotopes to "settle out". This causes a change in geometry and can misjudge the actual solution concentration. This has happened with ground water and other liquid samples, where solids settling out of solution have caused errors to occur.

e. Quality control issues

Detector efficiency and resolution need to be monitored to ensure that the detector is operating properly. For germanium detectors, the detector resolution tends to deteriorate before the detector fails. This is generally due to loss of vacuum in the detector cryostat. If the quality control system used detects such changes the detector can be repaired before a failure occurs. Also background levels need to be evaluated regularly to ensure that the counting system has not been contaminated.

f. Instrumental analysis

Many radioisotopes produce gamma rays and therefore can be detected using a gamma ray spectrometry system. Also many gamma ray emitting isotopes produce more than one gamma ray per decay. In addition, more than one isotope can emit gamma rays of similar energy, for example, ^{57}Co emits a 122.1 KeV gamma ray, ^{152}Eu emits a 121.7 KeV gamma ray and ^{154}Eu emits a 123.1 KeV gamma ray. These three energies are similar enough that they cannot be separated by evaluating that portion of the energy spectrum alone. All of these nuclides emit gamma rays of other energies. By looking for the other gamma rays, the presence or absence of each nuclide may be determined. This also makes it necessary to ensure that the energy calibration of the system is correct.

It is important to use a proper calibration when determining the energy calibration curve assigning energy to MCA channels. If the sample to be measured contains mixed fission products, then the energy calibration curve should be determined using a mixed fission product standard. Sometimes a good standard will not be available and the scientist will need to use a standard or a combination of standards to provide the calibration curve.

In the majority of detector systems, there is a minimum amount of time which must separate two events before the second event can be detected. This minimum separation is referred to as dead-time and is dependent on the physical nature of the detector and the response time of the associated electronics. At high count rates, dead-time losses can become severe. The detector system hardware and software can include correction for these losses, but these corrections are approximations of the actual losses. High dead-time adversely affects the system's resolution as peak broadening can occur at high count rates.

g. Data reduction

Most gamma spectrometry systems use vendor supplied software to identify peaks and to use the identified peaks to identify which isotopes are present in the sample. Some gamma spectrometry software uses a weighted average of the activity calculated from all of the gamma rays from a single nuclide. If one or more of these gammas comes from more than one isotope, it is possible for the final result to be distorted by one gamma ray. In other cases only the most abundant gamma ray is used. If this is the case, there may be an incorrect result reported if this energy is emitted by more than one isotope.

h. Instrumental "quirks"

When gamma rays interact with matter, scattering takes place and energy is lost by the gamma ray. The scattering process introduces a significant number of apparent lower energy gamma rays that can be counted by the detector. If there are a large number of high energy gamma rays, the scattered gamma rays can mask the presence of a lower energy gamma ray. In this way some low abundance isotopes may go undetected.

As the sample count rate increases, the "dead-time" (the time that a detector cannot process an incoming gamma ray) increases and the detector resolution deteriorates. The increase in the dead-time means that it takes longer to process a sample (when live time counting is used) or there are fewer counts during the count (when real time counting is used). As the resolution deteriorates some gamma rays that may have been separately detectable at low count rates are combined into a broadened peak at higher count rates. In addition, the change in the shape of the peak can affect the manner in which the software determines the peak energy, and can even think that there is more than one gamma ray under a given peak.

Despite the best stabilized power supplies, sometimes the center of a gamma peak will shift. One must watch for this as it throws the calibration off.

i. "Rules-of-thumb" and "common-sense-checks"

The software used to identify the presence of a particular isotope requires a library defining the isotopes of interest. When there is an unexpected isotope detected, it is sensible to make sure that the gamma rays detected for that isotope are present in the appropriate ratios. It could be that an isotope is identified as being present due to a gamma ray from a different isotope. It is also prudent to look at a list of gamma rays that are detected to make sure that some isotope not in the library has not been overlooked. This is particularly true when looking at spectra from samples of "fresh" fission products since there are often many isotopes present that are not normally identified.

j. Trouble-shooting and recovery methods

Changes in energy calibration can often be "fixed" by using a few known peaks such as the annihilation peak at 511 KeV and the ^{40}K peak at 1460.8 KeV to reset the calibration. Apparent changes in efficiency should be checked using a source. If the change is confirmed, previous counts since the last valid check should be repeated.

k. Identification of common experimental problems

Table 5 provided a summary of some experimental problems that are common to almost all experimental techniques and will not be repeated in this section. Table D-6 provides a summary of

common experimental problems unique to gamma spectroscopy. Note that this information is not inclusive of all possible experimental problems that may occur.

Table D-6: Summary of Common Gamma Spectroscopy Experimental Problems

Occurrence	Possible Cause(s)	Effect on Experimental Results	Possible Remedy
Check standard falls out of control chart acceptance band	• Change in instrumental operating characteristics since last calibration	• Results lower or higher than actual	• Recalibrate instrument
	• Instrumental problem affecting calibration	• Results lower or higher than actual	• Rerun calibration, trouble-shoot & repair as required
	• Compromised calibration standard	• Results lower or higher than actual	• Check calibration standard, replace if necessary
	• Improperly executed calibration	• Results lower or higher than actual	• Recalibrate instrument
Excessive dead-time corrections Excessive dead-time corrections *continued*	• Too high gamma count rate	• Results lower than actual	• Move the sample away from the detector or lower the sample concentration. Could use shielding between the sample and the detector, however, using shielding (e.g. lead) causes its own set of problems such as scattering and should be avoided unless there is no other alternative
Absorption of weak gamma rays	• Density of matrix miss-measured or improperly corrected	• Results higher than actual	• Re-measure matrix density or recalculate and perform correct calculation or change the sample geometry to a thinner geometry
Poor peak shapes	• Instrumental problem: vacuum failure, preamp resistor degradation, electrical pickup	• Results lower than actual	• Trouble-shoot & repair as required, then check calibration (evacuate chamber, thermal cycle the detector or/and replace preamp, check connections
	• High energy tailing	• Results lower than actual	• Check pulses at preamp – probably a detector/amp/preamp problem or neutron damage
Poorly resolved peaks	• Overlapping gamma emitters	• Results higher than actual	• Look at a different peak for that nuclide – may need to perform a chemical separation
Overlapping peaks	• Improper data reduction – not using "clean" gamma energy	• Results higher than actual	• Look at a different peak for that nuclide – may need to perform a chemical separation OR use peak de-convolution software
High background	• Contaminated detector	• Results higher than actual	• Clean, if does not remedy problem may need to replace components
	• High external background due to radioactive components near detector	• Results higher than actual	• Move components away from detector
	• Shield door left open	• Results higher than actual	• Close shield door
Sporadic noise	• Radio signal interference	• Results not discernable or consistent	• Put in place procedure (postings,

Occurrence	Possible Cause(s)	Effect on Experimental Results	Possible Remedy
in the spectrum			etc.) to prevent action
	• Dirty power – power hungry devices switching on and off	• Results not discernable or consistent	• Get a REALLY good power condition
	• Ground loop	• Results not discernable or consistent	• Shielding cables, change cable routes, remove CRT monitor
Low count rates for low abundance gamma emitters	• Presence of a large quantity of a gamma emitter	• Poor accuracy	• Separate out the high abundance gamma emitter and rerun a more concentrated sample to get better counting statistics
	• Background counted with sample in it	• Results lower than actual	• Re-run background and re-analyze

15. Thermal Ionization Mass Spectroscopy and Isotope Dilution Technique

Section VII.C.1 provides background and references for this technique. This method can be used for any multiple isotope elements and is particularly useful for elements compromised of stable isotopes which cannot be measured by radioactive counting techniques. Some elements are more challenging than others to analyze using this technique. For example, cesium is highly reactive and will burn out a Faraday cup. Highly refractory elements are tricky to analyze since they are difficult to ionize.

a. Analytes

Mass spectroscopy has been used to measure uranium, plutonium, neodymium, and samarium isotopes for physics irradiation test program samples.

b. Sample processing

Sample processing can be very complicated for this technique since it is necessary to isolate the element being analyzed in a highly purified state. The presence of other elements can reduce the ionization efficiency and/or result in mass interferences at the masses being measured. Many elements need to be in a specific chemical form for loading to optimize the ion current and ensure a stable ion beam.

c. Sample loading

As outlined in Section VII.C.1, tiny amounts of liquid sample are evaporated upon a thin ribbon filament. The filament is then placed in the source of the mass spectrometer and heated by running a current through the filament heating it to hundreds of degrees. This filament heating facilitates evaporation and ionization of the atoms of the element to be measured. The typical loading parameters are the chemical form of the sample solution, the filament material (very thin ribbons of high purity metals such as rhenium or tungsten), and the filament surface treatment (e.g. carbonization of the filament to lay down a layer of carbon over the filament surface to facilitate the ionization process). TIMS filaments can be of single, double and triple flat ribbon filament configuration, canoe shaped and other specialized shapes used in custom TIMS instruments. Some laboratories use an alternate practice of loading the sample on a single resin bead to provide a point source[q].

[q] This practice is typically limited to loading very small samples (e.g. environmental samples).

Over the years, mass spectrometrists have determined the optimal loading combinations to provide a stable, high intensity ion beam. Each laboratory establishes their own loading techniques that work best for their applications. Debates on which loading procedures are superior will not be covered in this appendix. The test sponsor needs only be aware that these possibilities exist and that the entire reason for these gyrations is to optimize the ionization of the element to be measured. For most elements, the loaded solution needs to be carefully processed because impurities can "poison" the filament surface, reducing the ionization efficiency.

d. Chemistry "quirks"

Plutonium chemistry is problematic since it readily forms a fluoride, likes to polymerize and adsorbs onto vessel walls. Many nuclear laboratories process large amounts of plutonium and contamination may easily affect trace plutonium analysis. IDMS measurements of ^{238}Pu can be compromised by incomplete uranium separation for samples containing high uranium concentrations.

Some analytes are difficult to separate from the major components of the test specimen which can result in a substantial isobaric interference.

Uranium results can be affected by contamination with ^{238}U from ordinary dirt (or/and ^{236}U, depending upon the composition of uranium processed in the subcontractor's facilities). ^{238}Pu is an isobaric interference and must be completely separated from the sample to provide good analysis.

Neodymium and samarium fission products are difficult to process: good separation from the other rare earth elements is vital to eliminate possible isobaric interferences.

e. Quality control issues

The largest contributors to the accuracy of any IDMS quantitative analysis method are the quality of the spike material and the availability of well characterized isotopic standards for instrument calibration. The quality of IDMS, as in all analytical methods, is dependent on the quality of the chemistry performed upstream of the process. Please refer to the sections discussing the dissolution process and addition of spike material

f. Instrumental analysis

Key elements for successful analysis via TIMS are similar for other instrumental methods: stable ion beam, proper calibration, stable magnetic field, low background, good peak shapes, stable, efficient detector response, and reliable data acquisition system. However, even with properly calibrated equipment run by a highly trained individual, poor results can be acquired if the sample is not properly prepared. TIMS analysis is very dependent on the quality of the chemical separation.

The major instrumental attributes and how they may affect the measurement quality are detailed in the following paragraphs.

- *Ionization efficiency*: The aforementioned painstaking loading procedures are required to maximize the ionization of the element to be analyzed. Ionization efficiency is simply the ratio of the ions formed to the number of atoms loaded onto the filament. The complicated part is that all the physics that occurs between the filament surface and the loaded element is not specifically known. Mass spectrometrists have determined mostly through trial and error what

configuration of filament material, treatment, and chemical form of the loaded element provides the best efficiencies. Note that these efficiencies are element dependent.

- *Mass fractionation*: Section VII.C.1 defined mass fractionation. For a given chemical element, heavier atoms require more energy to be atomized and ionized than lighter atoms. Thus, ions for the lighter isotope of a chemical element are more readily produced than the heavier isotopes. Mass fractionation is typically measured using a NIST isotopic standard. Mass fractionation per mass unit is calculated and the final data are corrected. The equation for mass fractionation corrections can be found in Appendix B. Mass fractionation values are a function of the chemical element, filament type, chemical form, and instrumentation. They can vary with time and must be measured for each set of analyses. Also note that mass fractionation can be called isotopic fractionation. In addition, there are other processes that may cause mass fractionation (improperly designed ion optics, certain detectors can have different responses as a function of mass, etc.), although TIMS instruments are designed to minimize mass fractionation from any other sources to be negligible compared to the phenomenon of ionization from the filament. Proper measurement of standards and properly executed mass fractionation calculations correct this effect which can significantly perturb the results.
- *Mass resolution:* The mass spectrometers used for physics irradiation test program samples have been low mass resolution instruments with a typical mass resolution of 400[r] which is enough to cleanly separate ions that differ by at least one atomic mass unit (amu). Low resolution instruments are most commonly used because they are adequate for most routine applications where the element is isolated from other interfering species. High resolution instruments are more expensive due to the components required to provide high mass resolution separation and trickier to maintain due to the higher requirements of all components. They typically have lower efficiencies since the required optics demand narrower optical slits in the ion optics to achieve higher mass resolution.
- *Isobaric interferences*: A problem inherent to all types of mass spectrometric techniques is mass interferences. These mass interferences are not restricted to isobaric interferences (^{238}U, ^{238}Pu) but can be molecular. For example, the $^{90}Zr_2$ dimer interference at mass180 or the hydride interference $^{238}Pu^{1}H$ with ^{239}Pu. Note that these molecular interferences are not necessarily chemically stable and any combination can occur to a statistically significant level. Oftentimes mass spectrometrist will measure an additional mass which monitors a common interference. For example, measure mass 239 along with the uranium isotopes to uncover a significant plutonium interference that could perturb ^{238}U results.
- *Source, ion optics, magnetic and detector stability*: Stability of the key components of the mass spectrometer is key to precise and accurate analysis. Fluctuations in the source current can change the ion beam current of the element being analyzed, fluctuations in the magnetic field can alter peak integration, and detector instability can perturb the measured signal.
- *Multiple detector issues* The beauty of multiple detector mass spectrometers is that they are not as sensitive to the system stabilities outlined in the previous paragraph. Since all masses are measured simultaneously, small fluctuations in ion beam current will affect measurements for all masses the same way for the same measurement. However, these systems have their own

[r] Calculated as M/ΔM where M is the measured integral mass and ΔM is the nuclide mass difference between the two species - for example: the required mass resolution to separate $^{238}Pu^{1}H$ and ^{239}Pu at mass 239 would be 239/(238.0495+1.0078-239.05216) = 46,498.

inherent problems which are discussed in the following *"Rules of thumb" and "common-sense checks"* section.

- *Ion counting versus analog counting:* TIMS data collected for physics irradiation test programs is typically performed using an analog counting detection system. A Faraday detector was used to measure the ion current and this current was converted to a voltage using a high precision resistor. The measured voltage for each mass was then recorded by the data acquisition system.

  In ion counting techniques, either an electron multiplier operated in ion counting mode[s] (see Section VII.C.1) or another ion counting detector is used where the output is the number of counts for each mass. This type of detection is also referred to as pulse counting. Ion counting systems are typically more complicated and as a result are more finicky than analog counters. However, ion counting systems can measure signals that are orders of magnitude smaller than analog systems. The low signal threshold that a Faraday cup analog system can measure is defined by the noise of the resistor that is used to convert the current to a voltage. High precision resistors are employed (some models cryogenically cool the resistor) to reduce the resistor's noise levels to their theoretical limits. However, the Faraday cup analog system is superior to ion counting systems in that they are more robust and can also measure higher ion currents without damage.

  In general, ion counting systems are used for environmental samples which tend to be very small and the Faraday analog systems are employed for large sized production samples.

g. Data reduction

Most TIMS software reports the data as atom ratios even though the instrumental readout for Faraday detectors is the voltage produced by the measured ion current. The processed data will frequently be provided as isotopic weight percents.

Data reduction for TIMS and especially for IDMS can be very convoluted. The reduction is not difficult mathematically, but there are multiple steps and many need to be made in a particular order. The test sponsor needs to know the exact identity of any given data set. For example, the subcontractor provides "raw" atom ratio data. How is "raw" atom ratio data defined for that subcontractor's instrument? Subcontractors may use software provided by the instrument's manufacturer, write their own software, or use a combination of both by modifying the manufacturer's software. Thus "raw" atom ratio data may provide atom ratios that are ratios of the currents with/without the multiple detector gain calibration and with/without mass fractionation corrections. It is important to understand which corrections have/have not been made to the data.

The test sponsor also needs to determine that all the appropriate calculations were made (see Appendix B). In isotope dilution, the contribution to each mass from the added spike needs to be appropriately backed out before reporting the final data. In addition, are the values blank corrected or was the blank deemed sufficiently low when compared to the sample and blank correction was not performed? It is imperative that the mass spectrometrist document the data reduction process for each experiment.

[s] Electron multipliers can be operated in either ion counting or analog mode.

h. Instrumental "quirks"

Most of the "quirks" in mass spectrometry are typically a result of chemistry problems. However, there are a number of instrumental quirks that can perturb results and be difficult to pinpoint.

Radio transmissions can cause havoc with the more sensitive ion counting systems. The effect is sporadic data that cannot be explained or reproduced. This is a difficult cause to pinpoint because the radio transmissions may not occur during the day. Most TIMS instruments run in a fully automated mode and samples are analyzed 24 hours a day. Facilities with off-hour security checks may find that anomalous data occur when the security officers "key" their radios during their night time inspections.

Another insidious problem can be fluctuations in the power supply that the power condition fails to remove thus affecting the sensitive electronics. These occurrences can be random and may be dependent on power-hungry equipment which cycles on and off.

Temperature and humidity can also be a player – not only in how fast the vacuum system pumps down after a sample changes, but also the stability of the electronics.

i. "Rules-of-thumb" and "common-sense-checks"

Mass spectrometry software typically calculates the experimental error of a measurement as the standard deviation of a set of calculated ratios. Each measurement is not a single measurement of all masses, but a repeated set of mass measurements. If the instrumentation is working properly, the experimental error should follow Poisson statistics. A good check of the measurement is to take the square root of the highest count rate and multiply by two. If measurement error as calculated by the software is much higher than this value, there is typically something wrong with the equipment (power supply instability, fluctuation in magnetic field, etc.)

In addition, because the experimental error is a function of the count rate, the expected precision is a function of isotopic abundance. The "rule-of-thumb" for uranium is:

- under 2 wt% => ~1%;
- 10 % => ~0.35%;
- 20% => ~ 0.25%; and
- 50% => ~ 0.15%.

If the expected precision is drastically different from this rule of thumb, it is a good bet that there is something wrong with the analysis with the cause being an instrumental problem, a sample processing problem, or a combination of both.

Multiple detector systems have an added degree of complexity because each Faraday cup has its own unique efficiency. This can cause a variety of problems that are not encountered when using a single detector where the magnetic field is switched to consecutively measure the ion current for each analyzed mass. Errors can occur if:

- the efficiency for any detector is incorrectly determined;
- there is a problem with one or more detectors (the more detectors, the more likely there will be a problem with one of them that may go unnoticed); and

- the detector efficiency calculation is performed incorrectly or uses the flawed detector efficiencies.

There is a way to easily check if the multiple detection system is working properly prior to performing the measurements. Perform the following sequence (order is not important) using a control sample having an isotopic composition similar to the analyzed sample:

- measure the required masses using one detector and switching the magnetic field (this is commonly referred to as "single collector mode");
- measure the required masses using the required detectors with a static magnetic field (this is commonly referred to as "static multiple collector mode"); and
- measure the required mass using the required detectors AND varying the magnetic field so that each mass is measured using each of the multiple detectors (this is commonly referred to as "dynamic multiple collector mode")

The resulting measurements for each mass should agree within the experimental uncertainties for all three modes. The test sponsor should request that this procedure be executed whenever multiple detectors are employed and the results documented in the final report.

j. Trouble-shooting and recovery methods

The documentation that is provided by the subcontractor is a vital component to being able to trouble-shoot and recover data from deviate analyses. Some problematic data cannot be salvaged after the fact, but others can. The following example illustrates a case where requesting the subcontractor to provide all data (including raw atoms ratios) was used to "salvage" data gone bad.

Quantitative isotopic uranium measurements were performed for fifty samples. To reduce cost, duplicate measurements were only performed for six of the samples. Duplicate measurements for ^{234}U, ^{235}U, and ^{236}U weight percents were in excellent agreement (0.5%) for a series of samples, but a portion of the ^{238}U duplicate measurements fell well outside of the technique specification's criteria that duplicate measurements should agree within 2%. Comparison of the experimental ^{238}U value to calculated values derived from physics models displayed a large discrepancy for the ^{238}U values but not the ^{234}U, ^{235}U, and ^{236}U values. The first investigation was to determine if there was ^{238}U contamination. There was a slight contamination, but the resulting data correction did not solve the variability. It was subsequently determined that the Faraday collector which measured mass 238 was intermittently unstable and needed replacement. Measurement of the uranium standard did not identify the instability in the detector used to measure mass 238 prior to analysis of the sample solutions. This oversight occurred because the subcontractor employed a uranium standard that was over 20% ^{238}U. The percentage present in the test specimens was 1-6%. Thus, the instability was not evident in measurement of the standard because of the higher concentration of ^{238}U. This clearly illustrates the necessity of either using a uranium standard with an isotopic composition which closely resembles the isotopic composition of the test specimen, or measuring a suite of standards with various isotopic compositions. For this example, all uranium data would be suspect if the only reported data was the total grams of uranium in the sample and the weight percents of ^{234}U, ^{235}U, ^{236}U and ^{238}U. An error in ^{238}U would be propagated to the other uranium isotopes since in order to calculate the weight percents all isotopes are summed together and then normalized to 100%. In this case the test sponsor requested the subcontractor to provide all raw

data from the mass spectrometer measurements: most importantly, the atom ratios and the information on the ^{233}U spike that was added to the sample for purpose of quantification. In this case, some data can be "salvaged" from the results. The exact weight of ^{233}U added to the sample is known. The mass spectrometry output provides the following atom ratios: $^{234}U/^{233}U$, $^{235}U/^{233}U$, $^{236}U/^{233}U$ and $^{238}U/^{233}U$. With these ratios, and knowing the exact quantity of the spike (^{233}U) added to the samples, the quantity of ^{234}U, ^{235}U and ^{236}U could be calculated[t] independently of the erroneous ^{238}U.

Ideally, TIMS samples should consist of only one element. However, in real life, incomplete separation can result in isobaric interferences at the masses of interest. An isobaric interference involving a component of the filament and/or solvent can also occur. Some isobaric interferences can be "monitored" by the measurement of a mass which corresponds only to the isobaric interference, and not to one of the masses of interest. For example, mass 235 can be used to monitor uranium contamination (or incomplete separation from samples containing large uranium concentrations) when analyzing plutonium at masses 238, 239, 240, 241 and 242. This is especially important when the analyte is in a significantly higher concentration than the concentration of the interference. Basic principles of chemical separation dictate that it is impossible for any separation to be 100.00000000% effective. There will always be a very small carryover of uranium in the purified plutonium sample. If the separation chemistry is effective, the carryover should be small compared to the concentration of the analyte. More information on isobaric interferences can be found in the ICPMS "Trouble-shooting" section.

k. Identification of common experimental problems

Table 5 provided a summary of some experimental problems that are common to almost all experimental techniques and will not be repeated in this section. Table D-7 provides a summary of common experimental problems unique to TIMS and IDMS. Note that this information is not inclusive of all possible experimental problems that may occur.

Table D-7: Summary of Common TIMS/IDMS Experimental Problems

Occurrence	Possible Cause(s)	Effect on Experimental Results	Possible Remedy
Check standard falls out of control chart acceptance band	• Change in instrumental operating characteristics since last calibration	• Results lower or higher than actual	• Recalibrate instrument
	• Instrumental problem affecting calibration (i.e. instable power supply, magnetic field, detector response)	• Results lower or higher than actual, erratic results	• Rerun calibration, trouble-shoot & repair as required
	• Compromised calibration standard	• Results lower or higher than actual	• Check calibration standard, replace if necessary
	• Improperly executed calibration	• Results lower or higher than actual	• Recalibrate instrument
	• Contamination	• Result higher than actual	• Determine contamination source and remedy

[t] There would also be other instrumental corrections that would be applied but this is the basic methodology.

Occurrence	Possible Cause(s)	Effect on Experimental Results	Possible Remedy
Low ion beam intensities and/or instable ion beams	• Presence of substance that poisons the filament and retards ion emission	• Poor precision due to low count rates	• Repeat chemistry
	• Incomplete separation and/or purification chemistry	• Poor precision and/or accuracy	• Repeat/refine chemistry
	• Improper loading procedure (wrong filament type, filament surface treatment,	• Low count rate producing poor precision	• Correct loading procedure
	• Filament movement resulting from softening of the ceramic holding the filament (can occur when very high filament currents are required to ionize a highly refractory element)	• Possibly affect precision	• Use ICPMS
	• Contamination burning off the filament	• Poor precision and/or accuracy	• Could allow to burn off, then take data – best to identify contaminate and remove prior to loading
Mass interference	• Incomplete separation and/or purification chemistry	• Result for isotope where interference occurs higher than actual and the results for the other isotopes may be perturbed to be lower than actual	• Identify problem and correct
	• Contaminated filament or sample loading reagent/equipment	• Result for isotope where interference occurs higher than actual and the results for the other isotopes may be perturbed to be lower than actual	• Identify source and correct
Poor peak shapes	• Poor mass resolution/magnetic drift	• Poor precision, possibility of affecting accuracy	• Check stability of magnetic field
	• Signal processing components	• Poor precision, possibility of affecting accuracy	• Check out all signal processing components
Unexpected atom ratios or poor precision	• Mass interference(s)	• Erroneous isotopic content for one or more isotopes	• Identify source and correct
	• Improperly calibrated multiple collectors	• Erroneous isotopic content for one or more isotopes	• Recalibrate detector system and check that all atom ratios agree using static, dynamic data acquisition modes
	• Noisy detector	• Erroneous isotopic content for one or more isotopes	• Check all detector responses and correct issue
	• Contamination	• Erroneous isotopic content for one or more isotopes	• Identify source and correct
Occasional erratic data	• Hiccup in electronics	• Poor precision due to dramatically different data from the rest of the data set – could affect accuracy	• Instrumental check out
	• Dirty power – power hungry devices switching on and off	• Poor precision due to dramatically different data from the rest of the data set – could affect accuracy	• Check status of power conditioner, determine if other high current-drawing equipment is on same electrical circuit
	• Radio signal interference	• Poor precision due to dramatically different data from the rest of the data set – could affect accuracy	• Procedurally restrict radio transmission during data collection

16. Inductively Coupled Plasma Mass Spectrometry Technique

Section VII.C.2 provides background and references for this technique.

a. Analytes

ICPMS has been used to measure ^{234}U, ^{235}U, ^{236}U, ^{237}Np, ^{239}Pu, ^{241}Am, ^{95}Mo, ^{97}Mo, ^{99}Tc, ^{101}Ru, ^{103}Rh, ^{133}Cs, ^{135}Cs, ^{139}La, ^{141}Pr, ^{143}Nd, ^{144}Nd, ^{145}Nd, ^{146}Nd,^{147}Pm, ^{147}Sm, ^{149}Sm, ^{152}Sm, ^{153}Eu, and ^{155}Gd[u].

b. Separation processing

Samples are typically diluted to reduce the matrix effects of dissolved solids and to reduce the maintenance caused by larger concentrations of analytes. It is difficult to accurately analyze an ion at low concentration after "flooding" the instrument with higher concentrations of the ion since background levels are elevated and sample introduction hardware can "bleed" the ion into the plasma causing carryover[v] problems.

One subcontractor performed no separation of the samples and merely performed a "dilute and shoot" procedure. Another subcontractor performed some separations to improve the results. For example, barium was separated to improve the ^{135}Cs measurement.

Separations may be performed for reasons other than isobaric interferences. Higher concentrations of dissolved solids can load down and change the ionization efficiency of the source. It is sometimes prudent to remove a major sample component that is not of interest so it does not impact the analysis of trace analytes.

c. Sample loading

The sample must be in solution. For typical physics irradiation test program experiments, the measured analytes existed in a much higher concentration than required by the ICPMS instrument. Thus the solutions were significantly diluted since high concentrations can plug the nebulizer. Typically the concentration of dissolved solids is maintained below 1000 μg/ml.

d. Chemistry "quirks"

The analyst needs to be aware of constituents that have the potential to drop out of solution before the sample is pulled into the nebulizer. Volatilization of components from the solution can also occur. For example, ^{129}I can volatilize when diluted with weak nitric acid.

e. Quality control issues

Many quality control ICPMS issues are very similar to those of TIMS. As in TIMS, a detector calibration is executed to track detector response and signal attributes. This is performed on a routine time interval.

A calibration that is not normally performed for a TIMS instrument but of great importance for ICPMS is a mass calibration over the entire mass range. Typical TIMS analysis involves measurements over a narrow mass range, since the element of interest is separated from the other

[u] This list of analytes is specific for the "dilute and shoot" method employed for these experiments. For example, ^{238}U can be measured via ICPMS if the uranium is separated from plutonium.

[v] Carryover is defined as traces of a constituent(s) from one sample remaining in the analytical system and affecting the analysis of the next sample.

sample constituents prior to analysis. The ICPMS calibration over the entire mass range is performed using a special mass calibration standard that covers the entire mass range (i.e. starting with lithium, boron etc. all the way up to uranium). Each instrument manufacture has specifications for each model on the calibration standard attributes, the routine for performing and calculating the mass calibration curve, as well as the required frequency of performing the mass calibration (typically every few months and whenever there is a significant instrument change). This mass calibration is a very similar technique to the energy calibration techniques used for gamma spectroscopy measurements.

The major difference between ICPMS and TIMS is that addition of an internal standard to the ICPMS sample solution is imperative to provide accurate results. This internal standard corrects for instrumental drifts, instabilities that occur from plasma and nebulizer effects, and differences in sample properties. For example, solutions of different acid concentration may have different viscosities which affect the ionization efficiency.

An internal standard must be chosen with care. The internal standard must not be in the sample and it is best if the standard is in the same mass range as the analyte of interest since there are mass bias effects and differences in ionization potentials.

To better understand the quality control aspects of ICPMS internal standards, it is useful to provide a general outline of a “typical” ICPMS analysis.

- First a blank solution containing a known amount of internal standard is run. A typical internal standard for samples containing uranium, transuranics and fission products is a combination of ^{115}In, ^{159}Tb and ^{209}Bi which are not present in any appreciable amounts in typical physics irradiation test program samples. ^{115}In (95.7% atom percent abundance) covers the low end of the typical fission product mass range. ^{159}Tb (100% atom percent abundance) covers the higher end of the typical fission product mass range. ^{209}Bi (100% atom percent abundance) is the highest mass suitable for the uranium and transuranic mass range. A typical added amount for this In/Tb/Bi internal standard mixture is 10 ppm for each nuclide and typically the same amount is added to each sample.
- The next sample to be run is a dilute standard solution containing the internal standard. The standard represents what is being analyzed in the solution. Oftentimes multiple internal standards will be employed to improve the analysis of multiple analytes. These standards are used for quantification of the data and account for the differences in mass bias effects and differences in ionization potentials.
- The next sample to be run is a more concentrated version of the standard solution containing the internal standard. Two different concentrations are run to account for differences that are a function of concentration.
- A rinse solution is then run through the ICPMS to clean out the source and prevent any sample carryover.
- Now the actual sample containing the internal standard is processed.
- The last step is to measure another aliquot of the blank solution containing the internal standard.

It is not unusual for ICPMS scientists to run multiple aliquots of the same sample to improve the overall accuracy of the results. One subcontractor performed two analyses for each sample: one for the fission product nuclides and a second run for the transuranic nuclides. They chose this method for two reasons: 1) significant concentration differences between fission product nuclide and transuranic nuclide sample sets; and 2) different standards were used for the fission product nuclide and transuranic nuclide sample sets.

As previously mentioned, usage of more than one standard is fairly common in ICPMS methods. Large differences in concentrations and also in various sample preparation dilutions drive the use of a variety of standards. Other considerations are that transuranic standards may contain other transuranic elements and common elemental impurities. For example, a uranium standard will not be mixed with a plutonium, americium, or neptunium standard because each standard may contaminate the other[w] and each of those may contain impurities such as iron, rare earths[x], noble metals, etc. It is more work running multiple standards, but the trade off is that there is more certainty in the amounts being calibrated for.

Hydride and oxide formation can result in mass interferences that increase the signal for a given isotope. The hydride formation for one subcontractor's instrument was small (0.05%) and not a problem for most analyses. However, the hydride formation can be troublesome for other analyses (e.g. trace plutonium (^{239}Pu) in uranium metal ($^{238}U^{1}H$)). A similar phenomenon exists for oxide formation which is typically 1 to 3%. An example of an oxide interference is $^{232}Th^{16}O$ and ^{248}Cm at mass 248.

Calibration across the mass spectrum can change from one instrument to another. For example one subcontractor's instrument displayed little/no mass bias in the mass range of barium isotopes (130s), but percent changes at the high mass end. The signal to concentration response from mass 134 to 138 was less than 1%, but between 234 to 238 could be several percent. This effect is different for different instruments.

Another consideration is the certainty of the known standard. The uncertainty in any given measurement is never better than the uncertainty of the calibration standard. This is true in any analytical technique, but this fact needs careful attention in the extensive use of standards in ICPMS methods.

f. Instrumental analysis

Many instrumental analysis issues are very similar to those of TIMS. The major difference between the two techniques occurs in the source (heated filament compared to high temperature plasma). The ICPMS technique is very susceptible to nebulizer and plasma effects. These issues are typically addressed through the proper selection of internal standards and use of calibration curves. The ICPMS techniques can also be matrix dependent: a slight difference in the sample matrix can cause considerable systematic error. Sample matrix effects can also be addressed using internal standards and calibration curves and also by matrix matching the samples. Matrix effects are typically observed for samples whose compositions differ significantly from one another. This situation did not occur for the analysis performed in recent experiments. The samples had nearly

[w] Note that ^{241}Am always has ^{237}Np in it, and ^{237}Np always has ^{233}Pa in it.
[x] Rare earths have isobaric interferences and must be separated for calibration if they are present.

identical major component concentrations while the dramatic concentration differences occurred in the very minor components.

Exact methods for reducing nebulizer and plasma effects are very dependent on the sample composition and the type of ICPMS. TIMS instruments have a very standard configuration with the differences being in the "bells and whistles" (i.e. number of filaments the source can accommodate, multiple detector system, etc.). ICPMS instrument configurations are not as standardized. For example, different types of nebulizers and/or sample introduction systems are available. The procedure for addressing nebulizer effects will be dependent on the type of nebulizer. All commercially available TIMS instruments use the same type of source: heated filament.

Section VII.C.2 stated that many ICPMS instruments employ electron multiplier detectors which can be operated in both ion counting and analog detection modes. Most ICPMS scientists prefer to stay in ion counting mode since the "crossover" between the two modes has to be carefully calibrated to obtain good results. They achieve this by performing additional dilutions for major components.

Ideally ICPMS should provide accurate measurements for dozens of analytes from a single solution that required little chemical processing. However, some chemical processing is often required to improve accuracy for certain constituents. The exact method is dependent on the ICPMS instrument configuration, sample composition and the knowledge and experience of the scientist.

g. Data reduction

As seen in the provided example demonstrating how ICPMS samples are run, there are many corrections to be performed. Some matrices require excessive use of internal standards and calibration curves. As in IDMS, the appropriate calculations must be performed correctly.

Data output is typically provided as microgram per liter and sometimes errors are made in converting these values to microgram per gram of sample.

h. Instrumental "quirks"

As explained in Section VII.C.2, most ICPMS instruments use electron multipliers which can be operated in two different modes: ion-counting mode for low signals, and analog mode for larger signals. Most ICPMS software automatically switches between these two modes where the mode selection is a function of the signal magnitude. The analyzed samples covered a large concentration range. If the signal magnitude fell on the boundary between these two detection modes the data would be erratic. This problem was remedied by performing a different dilution of the solution so the signal would be measured fully in one detector mode.

Another annoying "quirk" that is specific to the ICPMS technique is that some heavy elements (i.e. uranium) will transfer an electron to an easily ionized atom (i.e. potassium) resulting in signal suppression. This effect can be addressed by chemical processing the sample solution prior to analysis.

i. "Rules-of-thumb" and "common-sense-checks"

The measurement of multiple species in one analysis provides "common-sense-checks" that cannot be used in TIMS where only one element is analyzed. The analyst can use fission product yields to

check the relative concentrations between analytes: calculated ratios for "pure[y]" fission products should correspond to the ratio of the measured fission products.

Isobaric interferences have been discussed in the thermal TIMS technique section. The same concepts apply to ICPMS, however, the problem is more prevalent in ICPMS techniques since little or no chemical separations are performed and most samples contain multiple analytes. This section provides additional "common-sense-checks" to investigate isobaric interferences. Remember that typically ICPMS instruments provide data for the entire mass range, while TIMS typically provides data for a limited mass range. The same techniques described here can be used for the TIMS technique.

Always calculate the mass of commonly occurring isobaric interferences (i.e. oxides, hydrides, argides[z]) and check the corresponding mass for a peak. If there is no peak, the interference is not present. Hypothetical example: check mass 195 to see if there is an argide interference (e.g. ^{195}Pt-^{40}Ar) at mass 235.

- If there is no peak, there is no platinum present. If there is a peak, check the masses for the other major isotopes of platinum (194, 196 and 198) for peaks.
- If there are peaks at those masses, check to see if the isotopic abundances check out (194 = 32.9%, 195 = 33.8%, 196 = 25.3% and 198 = 7.23%).
- If the abundances check out, look for the two minor isotopes at masses 190 and 192 which should be present with isotopic abundances 0.13% and 0.78% respectively.

If the above checks are positive, then not only does mass 235 have a possible isobaric argide interference, but also masses 234, 236, and 238 will have the corresponding isobaric platinum argide interferences. Note that the presence of these peaks does not prove the existence of an isobaric Pt-Ar interference at mass 235, only that the possibility exists.

One should note that some interferences that form on a TIMS may not form on an ICPMS. One theory is that the ICPMS plasma is significantly hotter than the temperature of a TIMS filament and blows some common TIMS molecular interferences apart.

Fission product yields can also be used as a "common-sense-check". For these physics irradiation test program samples, the transuranic nuclides are predominantly formed by neutron capture from uranium. Thus the amount of transuranic concentrations should decrease with increasing transuranic atomic number[aa]. This leads to another "rule-of-thumb" that transuranic nuclide concentration will decrease approximately one order of magnitude with each increase in Z. For example, if the sample has a plutonium concentration of 1000 ppm, the americium concentration will be approximately 100 ppm and the curium concentration with be approximately 10 ppm. Note that this "rule-of-thumb" is half-life dependent and will change with increasing time since the end of the irradiation process. Radioactive decay also needs to be taken into consideration. The end user also needs to be aware of which nuclides build up due to radioactive decay of other nuclides (i.e. ^{241}Am from decay of ^{241}Pu).

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[y] A nuclide that is produced as a fission product, that is not initially present in the unirradiated sample, and is not a product of another nuclear process (i.e. nuclear decay of another species).
[z] Argide interferences are typical in ICPMS since the majority of instruments use argon plasmas.
[aa] Decay has to be accounted for properly for this method to make sense.

j. Trouble-shooting and recovery methods

The proceeding section illustrated that dealing with isobaric interferences is a complicated and tricky business. The good news is that some isobaric interferences can be corrected for. For example, ICPMS is a quite easy way to perform uranium analysis. However, if the sample contains any plutonium, the ^{238}U data are jeopardized by ^{238}Pu. Plutonium can be measured independently by separating the plutonium from the sample and performing an independent analysis. The plutonium results provide the amount of ^{238}Pu present in the sample which can be subtracted from the ICPMS ^{238}U data to provide the corrected uranium data. You may ask why bother? Why not just separate out the uranium in the first place? This approach is very helpful when analyzing a large number of analytes in the same sample. For example, suppose the purpose of the experiment is to provide quantitative analysis of uranium, plutonium and a variety of fission products. Typically TIMS could be used to provide the uranium and plutonium data, and ICPMS could be used for all the required fission products. However, uranium could also be analyzed by ICPMS and corrected using the TIMS plutonium data which would reduce the number of analyses by 34%. The cost savings would be greater than 34% because the TIMS uranium separation is very laborious.

k. Identification of common experimental problems

Table 5 provided a summary of some experimental problems that are common to almost all experimental techniques and will not be repeated in this section. Table D-8 provides a summary of common experimental problems unique to ICPMS. Note that this information is not inclusive of all possible experimental problems that may occur.

Table D-8: Summary of Common ICPMS Experimental Problems

Occurrence	Possible Cause(s)	Effect on Experimental Results	Possible Remedy
Check standard falls out of control chart acceptance band	• Change in instrumental operating characteristics since last calibration	• Results lower or higher than actual	• Recalibrate instrument
	• Instrumental problem affecting calibration (i.e. instable power supply, magnetic field, detector response)	• Results lower or higher than actual, erratic results	• Rerun calibration, trouble-shoot & repair as required
	• Compromised calibration standard	• Results lower or higher than actual	• Check calibration standard, replace if necessary
	• Improperly executed calibration	• Results lower or higher than actual	• Recalibrate instrument
	• Contamination	• Result higher than actual	• Determine contamination source and remedy
Low ion beam intensities and/or unstable ion beams	• Low analyte concentration	• Poor precision due to low count rates	• Adjust
	• Poor sample introduction: nebulizer problems, plugged sampler/skimmer cones, spray chamber not draining	• Poor precision with erratic results	• Proper maintenance and check out of sample introduction system
	• Improper tuning of ion lenses (tune on a high mass and measure a low mass)	• Results higher or lower than actual	• Follow proper ion lens tuning for the mass range to be analyzed
	• detector problems (detector	• Results lower than actual	• Verify detector characteristics and

Occurrence	Possible Cause(s)	Effect on Experimental Results	Possible Remedy
	not on "plateau")		correct as needed
Poor peak shapes	• Poor mass resolution/magnetic drift	• Poor precision, possibility of affecting accuracy	• Check stability of magnetic field
	• Signal processing components	• Poor precision, possibility of affecting accuracy	• Check out all signal processing components
Unexpected atom ratios or poor precision	• Mass interference(s)	• Result for isotope where interference occurs higher than actual	• May need to perform some separation chemistry or measure a mass of the interfering element in order to provide a correction
	• Switching over between analog and pulse counting detector modes	• Poor precision and possibly erroneous data	• Adjust dilution so that repeat measurement can be made so that the detector is run in one detector mode
	• Noisy detector	• Poor precision and/or erroneous data	• Check all detector responses and correct issue
	• Contamination	• Erroneous isotopic content for one or more isotopes	• Identify source and correct
Occasional erratic data	• Hiccup in electronics	• Poor precision due to dramatically different data from the rest of the data set – could affect accuracy	• Instrumental check out
	• Dirty power – power hungry devices switching on and off	• Poor precision due to dramatically different data from the rest of the data set – could affect accuracy	• Check status of power conditioner, determine if other high current-drawing equipment is on same electrical circuit
	• Radio signal interference	• Poor precision due to dramatically different data from the rest of the data set – could affect accuracy	• Procedurally restrict radio transmission during data collection

17. Inductively Coupled Plasma Atomic Emission Spectrometry Technique

Section VII.D provides background for the technique. One subcontractor used ICPAES to measure ^{139}La and ^{99}Tc. ^{139}La and ^{99}Tc are mono-isotopic in these samples and could be analyzed using ICPAES. ^{139}La and ^{99}Tc were also measured using ICPMS and the subcontractor determined that the ICPMS results were superior.

The discussion of this technique is abbreviated due to the limited use of ICPAES in recent experiments. ICPAES has issues that are common with ICPMS in that they share the same mode of sample introduction and ionization. Thus the same nebulizer and plasma related effects occur in both ICPMS and ICPAES techniques. As in ICPMS, internal standards are extensively used in ICPAES.

There are other issues that are unique to ICPAES since it is not a mass spectrometry technique and it measures the atomic emission spectrum of the analyzed sample. Emission line drift is a common problem associated with ICPAES instruments. This problem is addressed by controlling the temperature and pressure of the spectrometer. Proper ventilation to remove excess heat is imperative. Emission line drifts are monitored by the periodic analysis of a known calibration standard that is run periodically throughout the analysis.

ICPAES analyses can also be affected by concentrations of other analytes present in the sample solution. The subcontractor routinely analyzed samples for technetium and lanthanum. Typically these analytes are measured in solutions containing high concentrations of plutonium. The high

concentration of uranium and the low technetium and lanthanum concentrations in physics irradiation test program samples resulted in perturbed ICPAES technetium and lanthanum results. The subcontractor had not encountered this problem in previous work and investigated this perturbation. The developmental work revealed that the signal from technetium and lanthanum were biased significantly when significant uranium concentrations were present. For example, uranium concentrations of 5,000 ng/mL can cause a negative bias of about 50 ng/mL for lanthanum, and uranium concentrations of 10,000 ng/mL can cause a positive bias of about 35 ng/mL for technetium. The analysis perturbation may become significant for low concentrations of technetium or lanthanum (about 300 ng/mL). An alternative to performing a time consuming uranium extraction is to examine another lanthanum line at 408.672 nm. This emission line is not affected by uranium until its concentration exceeds about 100,000 ng/mL. The disadvantage of this line is its lower sensitivity: larger amounts of lanthanum need to be present to get a good quantifiable value.

18. Errors in the Data Reduction Process

There are a number of common problems that occur from errors in the data reduction process. Table D-9 summarizes some of these errors. This is of course not a complete listing but is provided to provoke the test sponsor AND end user to carefully consider the connectivity of the experimental parameters with the end product.

Table D-9: Common Data Reduction Problems

Occurrence	Effect on Experimental Results
Wrong dilution factor	• If dilution factor is too low, the results will be higher than actual • If dilution factor is too high, the results will be lower than actual
Blank correction error	• If correction is not made and is significant, results will be higher than actual • If the correction is too high, results will be lower than actual
Decay correction error	• If not made, or the correction is too small, results will be lower than actual • If the correction is too large, results with be higher than actual
Build-up from a decay product correction error	• If not made, or the correction is too small, results will be higher than actual • If correction is too large, results will be lower than actual
Improper instrumental corrections	• There are a vast number of these (detector efficiency, fractionation, etc.) and are too numerous to list – it is an exercise for the reader to determine the affect
Wrong units used	• Complete chaos ensues

19. The Complicated World of Nuclear Physics

Uranium fission is a simple concept. The reality of measuring the process's end products can be quite complicated. The isotopic content of the uranium changes, fission products are produced as well as transuranic nuclides, some having complex parent/daughter relationships. This results in the analysis of nuclides where many are interconnected. The experimentalist needs to consider these facts when performing such a complicated experimental measurement program.

a. Fission Products

There are over one hundred fission products resulting from uranium fission. Some fission products have very short half-lives and are completely decayed away prior to radiochemical analysis. A number of fission products are stable. Some fission products are nuclearly "transparent" and do not significantly react with neutrons, others are significant neutron absorbers.

There are some elements that have a large number of fission isotopes. For example, the samarium fission product has eight isotopes with six being stable. In general, fission products are fairly straight forward: they are easily decay corrected with the most annoying analytical difficulty being the large number of isobaric overlaps. Example isobaric overlaps are: ^{147}Pm & ^{147}Sm, and ^{155}Eu & ^{155}Gd. These overlaps result in some elements needing to be individually isolated and measured. Chemical separation of rare earth element fission products such as neodymium and samarium is very difficult and requires good radiochemical methodology and flawless execution.

b. Transuranic Nuclides

Neutron capture of uranium results in the formation of a large number of transuranic nuclides. These transuranic nuclides have similar experimental issues as the fission products: some have decayed away, and a large number of isobaric overlaps occur in some mass regions. However, certain characteristics of transuranic nuclides make them more difficult to measure. Americium and curium are very difficult to separate.

In general, the transuranic nuclides are subject to more nuclear processes (i.e. alpha decay, spontaneous fission) and many have complicated parent daughter relationships. Some nuclides not only decay, but are also produced from another nuclear reaction. For example, ^{241}Am is produced from the decay of ^{241}Pu. The interconnectivity of many of the transuranic nuclides demands careful consideration of decay and build-up mechanisms.

There are numerous isobaric interferences (i.e. ^{243}Am & ^{243}Cm and ^{238}Pu & ^{238}U) for mass spectrometric analysis techniques, and also a number of energy overlaps for alpha spectrometric measurements (i.e. ^{243}Cm & ^{244}Cm and ^{239}Pu & ^{240}Pu[bb]) resulting in the necessity of challenging radiochemical separations. Separation chemistry for many of the transuranic elements is very difficult.

Some nuclides are indirectly determined by the measurement of their daughters. For example, ^{243}Am is measured using gamma spectroscopy measurements of the ^{239}Np daughter. The same technique can be used for ^{237}Np where the ^{233}Pa daughter is measured via gamma spectroscopy. If the parent has been separated from the daughter, a sufficient time period must be allowed to pass before there is enough daughter build-up for a successful measurement. Remember that many

[bb] This phenomenon also occurs for uranium: ^{233}U and ^{234}U.

parent/daughter transuranic relationships consist of a short-lived daughter in radioactive equilibrium with a long-lived parent where both nuclides decay with the parent's half-life (see Reference 1). The daughter's half-life may indicate that the daughter has decayed away, but it actually has not because of this equilibrium state with the parent.

20. Test Specimen Composition Impact on Experimental Methodology

After years of development and practice, the experimental program has all the bugs worked out and the subcontractor is fairly confident in processing the irradiated test specimens. Then the composition of the test specimen is changed. Even a seemingly small change in the test specimen composition can cause some significant changes in the experimental process. This may result in some analyses being easier to perform and others becoming more difficult. Potential interferences that could be negligible for one test specimen composition may become significant and require changes in the radiochemical methodology. Additional analyses may be needed as confirmatory checks that the methodology is still producing accurate analyses and/or providing data to allow for corrections. Test specimen composition changes can be grouped in two categories: elemental composition and ^{235}U enrichment.

a. Test Specimen Elemental Composition Changes

Elemental composition changes can have a number of potential impacts and must be considered. Test specimen trace element concentrations can have an impact on the end results and require different methodology. For example, the previous sample composition had no significant neodymium content. The new test specimen has significant neodymium concentrations which affect neodynium fission product analysis of the irradiated test specimen.

Trace elements that are not among the nuclides being measured may also have an impact. The nuclide may provide an isobaric interference that can impact mass spectrometric analysis. The activation product of that nuclide could potentially interfere in radioactive counting techniques.

Concentration changes of elements in the original test specimen can impact accurate analyses. For example, increased iron concentrations may cause a problem in the separation chemistry or increase co-precipitation resulting in pulling analytes out of solution. All compositional changes need to be carefully examined.

b. Test specimen ^{235}U enrichment changes

Uranium enrichment variations can have significant impact on the radiochemical methodology. Table D-10 provides some major analytical and physics differences between low and high ^{235}U enrichment test specimens. For the purposes of this exercise, high enrichment is defined as greater than 90% weight percent ^{235}U and low enrichment is defined as less than 10% weight percent ^{235}U. This table does not include all effects and encourages the test sponsor to think about all possible differences that may occur for irradiation test specimens with differing ^{235}U enrichments. Even slight enrichment changes can affect the analytical process.

Table D-10: ^{235}U Enrichment Effects on Experimental Methodology

Measurement Group	Higher Enrichment ^{235}U (for example, >90%)	Lower Enrichment ^{235}U (for example, <10%)
Fission Products (FP)	• FP production is fairly straightforward with FP production following ^{235}U fission yields.	• If any significant power is produced by ^{239}Pu, FP production is more difficult to de-convolute since the FPs can be produced not only by ^{235}U fission, but also ^{239}Pu fission which has a different set of fission yields.
Uranium (U)	• Natural uranium contamination can have a significant impact on ^{238}U concentration measurements; however, low ^{238}U concentrations make it relatively easy to detect when the sample is contaminated with natural uranium. • Conversely, small amounts of enriched ^{235}U contamination typically will have low impact on ^{235}U concentration measurements; however, high ^{235}U concentrations make it more difficult to detect when the sample is contaminated with enriched ^{235}U (a common cross-contamination issue). • Monitoring mass 235 when measuring plutonium is a sensitive check for uranium carryover in the plutonium separations due to a high ^{235}U/^{238}U ratio.	• High ^{238}U concentrations make it more difficult to detect when the sample is contaminated with natural uranium; however, natural contamination has a much lower effect on the ^{238}U measurements. • Conversely, low ^{235}U concentrations make it easier to detect when the sample is contaminated with enriched ^{235}U (a common cross-contamination issue), however, small amounts of enriched ^{235}U contamination will have high impact on ^{235}U concentration measurements. • Monitoring mass 235 when measuring plutonium is not as sensitive a check compared to high enrichment ^{235}U samples for uranium carryover in the plutonium separations due to a lower ^{235}U/^{238}U ratio. However, the check is still useful to execute.
Transuranic Species (TRU)	• Samples typically have significantly lower TRU concentrations than low ^{235}U enrichment test specimens since there is little (1-5 weight percent) ^{238}U in the pre-irradiated test specimen. There are typically little TRUs formed above ^{244}Cm simplifying the analytical and data reduction processes. ^{242}Am and ^{243}Am are typically below detection limits.	• Samples have significant amounts of TRU concentrations with significant amounts being formed above ^{244}Cm which complicates the analytical and data reduction processes. Many TRUs are tricky to separate from one another for accurate measurements. This fact applies both to radioactive counting and mass spectrometric analytical techniques.

Please note that unintentional changes in the pre-irradiated test specimen can occur. For example, manufacturers may change their starting materials or their process. Careful monitoring of pre-irradiation test specimens is vital to the overall experimental quality.

21. So What Happens When Things Go Wrong?

DON'T PANIC! There are opportunities to creatively salvage experimental data provided that the test sponsor understands the entire experimental process and the quality control program, and requests that the subcontractor provide all acquired data instead of a portion of it. This may enable the knowledgeable test sponsor to "save" part of some analyses. Some problematic data cannot be salvaged after the fact, but others can.

It can also be very beneficial for the end user to look at the data in a different way. For example, suppose there is an unknown bias in the sampling method resulting in variation in the sampling volume. This would affect the quantitative results which are a combination of absolute measurements (total grams of the analyte in the sample) and relative measurements (isotopic weight percents). If there is a problem with the total grams of analyte measurement, the isotopic weight percents are still valid data and can be used. Perhaps the end user could use ratios, either isotopic ratios or ratios of the analyte to a specific nuclide (i.e. ^{235}U), to achieve their end goals. Depending on the data's end use, this approach may or may not be applicable. This is an example of why it is smart to have the subcontractor report ALL data (it costs little since they had to measure it so that they could calculate the quantitative results) and that creativity may be used to salvage some results in the event of an experimental problem.

Very often an analyte is measured by more than one technique and can be cross checked, or a problem with one analytical technique can be solved using measurements from another technique. For example, suppose an ICPMS measurement of uranium isotopes has a problem with the ^{238}U measurement due to the ^{238}Pu isobaric interference. TIMS/IDMS measurements of plutonium measurements can be used to determine the contribution of ^{238}Pu and be used to correct the ^{238}U. Don't view the analyses as individual pieces – they are interconnected and the entire suite of measurements can be used to sort out problems.

Don't forget that your test performers are your best source of expertise. They can be contacted even after the experiment's completion to discuss problem-some data and suggest possible solutions.

Also, don't be concerned if you see negative numbers for a measurement. This is a result of measuring a value at, or below, the detection limit of the technique (i.e. measurements of process blanks, or a species that has virtually decayed away). For example, if a gamma spectrometer has a background with no sample in the detector, the reported measurement can be a positive number when there is an indication of a peak. There is often a 1464 KeV peak due to ^{40}K in the background. Since this value is variable, when it is subtracted from a small quantity of ^{40}K present in the sample, the result can be negative. The detection limit is then governed by how many additional counts are needed before a real peak can be detected. This number represents the detection limit of the instrument. The reported value for the measurement is the measured value minus the background. When measuring at background levels, it is not unusual to obtain negative values after background correction. It is a statistical reality that a distribution for background corrected measurements of the blank minus the background measurement will include positive and negative numbers that, when averaged, approximate the detection limit. Since all instruments have some noise (background), the ability to determine that there is no analyte present is limited by the noise. This is then an approximation of the instrument's detection limit.

22. Summary

Various types of physics irradiation test program samples have been analyzed over the last several decades. As repeated over and over again in this document, this work is comprised of difficult analyses performed on complex samples. It is imperative to provide the information in this document to the subcontractor performing this work. This allows use of documented lessons learned and other information in aiding the scientist to avoid common pitfalls when performing these difficult measurements. The information is also valuable if the laboratory is developing new, improved

measurement methods. Remember that communication is key to the experiment's quality. Test sponsors need to communicate directly to test performers with no intermediaries.

Remember that modern analytical techniques will always provide a number. It is up to the test sponsor to determine if this number is sensible.

The field of radiochemical analysis, as in any scientific or technological field, is rapidly evolving. Better techniques will replace older methods and instrumentation breakthroughs will reduce the task of the separations radiochemist. The underlying principles of good sample preparation and analysis will never change in that the methods need to be appropriately designed and executed, with appropriate quality assurance measures.

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