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Handbook of Nuclear Safeguards Measurement Methods

Monsanto Research Corp., Miamisburg, OH

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The scope of this handbook includes applicable bulk measurements, chemical assay, passive nondestructive assay (NDA), and active NDA methods for all uranium- and plutonium-bearing materials routinely encountered in U.S. nuclear facilities, including feed and source materials, intermediate and final products, recycled materials, inventory materials, scrap and waste, measured discards, and process equipment holdup material. The information presented is mostly concerned with specific applications and performance of measurement methods, the factors that impact performance, and other considerations related to method selection or evaluation.

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Preface

Nuclear safeguards designers, measurement scientists, and managers are faced with the imposing task of selecting, implementing, and evaluating measurement methods for the wide range of special nuclear materials (SNM) being processed. The effectiveness of material control and accounting (MC&A) systems to detect critical losses of SNM depends greatly on the performance of the measurement methods that they select for each application. Unfortunately, safeguards designers and engineers have often lacked access to data on applications and performance. Information has been widely scattered throughout the scientific literature, monographs, and Government reports. Field experience with the methods used in routine production has only rarely been reported.

The Nuclear Regulatory Commission (NRC), Office of Standards Development, has long recognized the need to bring measurement data and information together in the form of a reference book for NRC and the nuclear industry. This handbook, commissioned by NRC, was prepared in response to that need. (Although this book was commissioned by NRC, the contents are the responsibility of the editor and may not reflect NRC regulations, rules, or policies.) It is intended to be a guide to the selection of methods for meeting specific measurement requirements, not a treatise on measurement. Information contained here on the methods, their applications, and performance was compiled from three surveys: a survey of production facilities (users' survey), a survey of the literature, and a survey of current exchange programs.

The survey of production facilities was conducted by visiting 22 U.S. Department of Energy (DOE) and commercial nuclear fuel production facilities and evaluating the methods used at each:

DOE Production Facilities

Hanford Engineering Development Laboratory, Richland, WA
Idaho Chemical Processing Plant, Idaho Falls, ID
Idaho National Engineering Laboratory, Idaho Falls, ID
Mound Laboratory, Miamisburg, OH
Oak Ridge Gaseous Diffusion Plant, Oak Ridge, TN
Paducah Gaseous Diffusion Plant, Paducah, KY

Portsmouth Gaseous Diffusion Plant, Piketon, OH
Rockwell Hanford Operations, Richland, WA
Rocky Flats Plant, Golden, CO
Savannah River Plant, Aiken, SC
Y-12 Plant, Oak Ridge, TN

Commercial Production Facilities

Babcock and Wilcox Co., Apollo, PA
Babcock and Wilcox Co. (Navy), Lynchburg, VA
Combustion Engineering, Inc., Hematite, MO
Combustion Engineering, Inc., Windsor, CT
Exxon Nuclear Co. Inc., Richland, WA
General Atomics Co., San Diego, CA
General Electric Corp., Wilmington, NC
Rockwell International Corp., Canoga Park, CA
Westinghouse Electric Corp., Columbia, SC
Westinghouse Electric Corp., (Cheswick), Pittsburgh, PA
United Nuclear Corp., Uncasville, CT

The survey included bulk measurements, chemical assay, sampling techniques, isotopic measurements, passive nondestructive assay (NDA), and active NDA methods used on all types of SNM processed; however, the survey included only methods used in routine production and evaluated with a documented measurement control program.

The most frequently used method for MC&A in current operations at the facilities visited was a combination of bulk measurement (usually weight), sampling, chemical assay, and isotopic measurements. This is especially true for main stream materials (feed, intermediate products, clean recycle materials, and final products), which account for more than 90% of the SNM being processed. Because these main stream materials are generally pure, well characterized, and homogeneous, they can be adequately sampled with simple physical sampling techniques. The chemical assay techniques are generally more precise and accurate than NDA methods. Because sampling and destructive analytical techniques are usually required to verify chemical composition, impurities, and structure characteristics, for process and quality control reasons, the additional samples required for SNM chemical assay apparently do not significantly increase waste streams.

Nondestructive assay techniques are used mainly for scrap and waste and other materials that are difficult to sample, dissolve, or analyze. These methods measure total SNM content of vessels, and, because they are usually rapid, all vessels in a flow stream can be measured. The NDA methods are in general less precise and accurate than chemical assay (except where sampling error renders chemical assay ineffective); therefore, they are not frequently used to measure mainstream materials. Two notable exceptions are (1) the use of calorimetry for mainstream and sidestream plutonium materials, with performances approaching chemical assay, and (2) rod scanners to verify fissile content of product fuel rods for quality control and safeguards purposes. As better standards are developed, NDA methods will no doubt be used more frequently to measure mainstream materials, especially if near real-time accounting is required.

Literature surveys for this handbook were performed by Science Applications, Inc. (bulk and active NDA methods), IRT Corp. (passive NDA methods), and Los Alamos National Laboratory (chemical assay methods) on those methods identified by the users' survey as well as on other methods that might be used for safeguards purposes in the future. References to this literature are cited in this handbook to guide the reader to more detailed accounts of the methods and procedures for their implementation.

There are several exchange programs that currently circulate SNM samples among the uranium and plutonium facilities for comparison of assay values. The purpose of these exchange programs is to identify unknown biases in the assay methods used at the participating facilities. Chemical assay and destructive isotopic abundance measurement methods are most frequently tested by the current exchange programs. Recently, however, weight measurements (UF_6 cylinders) and NDA methods (calorimetry) have been included.

The information and data collected from these three surveys were evaluated and then organized into the format of this handbook. The organization of the handbook is intended to permit the reader to evaluate quickly the potential measurement methods for meeting specific applications. Chapter 1 describes this organization and the recommended use of the handbook.

Collecting, evaluating, and compiling the vast amount of data and information presented here was an arduous and often tedious business. Clearly, such a sizable project was not completed without the assistance, advice, and support of a great many individuals to whom I owe a great debt of gratitude.

Ralph J. Jones and Philip Ting of the NRC Office of Nuclear Regulatory Research recognized the need for this book and proposed the project. W. B. Brown, J. E. Kent, Frank P. Gillespie, and Sandra Frattali, all of the NRC Office of Nuclear Regulatory Research, supported the project with capable assistance and considerable patience. Dr. Frattali, who was the program monitor during the preparation of the manuscript, read the many drafts of the book and provided useful comments and suggestions.

PREFACE

James Partlow and Edward McAlpine of the NRC Office of Nuclear Safety and Safeguards made a large amount of information available to us and helped arrange visits to the commercial facilities.

The DOE Office of Safeguards and Security and the various DOE operations offices assisted in arranging visits and collecting data at the DOE production facilities. I am grateful for this assistance and encouragement.

James Charles (Y-12 Plant), Robert Carpenter (Rocky Flats Plant), and David Lund (New Brunswick Laboratory) supplied data and information from the exchange programs. Leslie G. Fishbone (Brookhaven National Laboratory) kindly supplied me with an advance copy of his publication, "Safeguards Instrumentation, A Computer-Based Catalog," from which I extracted useful data and information.

Because of the importance of the users' survey information and data, I would like to express my thanks to the managers, measurement scientists, and statisticians at the production sites visited. They gave unselfishly of their time and shared their experiences and data with us. Though I cannot identify each one, I am grateful to all.

Thanks is also due the staff members of the Office of Nuclear Safety and Safeguards, the Office of Inspection and Enforcement, and the NRC regional offices for their review of the manuscript and their suggestions for revisions.

No volume this size was ever completed without a great deal of eye strain and hard work. The assistance and cooperation given me by technical editors Marjorie F. Hauenstein and Stephen Nowka, word processors Nancy A. Panella and Jamie A. Landrum, and librarian Sue Moore, all of Monsanto Research Corp., are deeply appreciated.

If this handbook eases the burden of method selection and contributes to improved nuclear safeguards, then all our efforts will have been worthwhile

Donald R. Rogers
Miamisburg, Ohio

Acronyms and Initialisms

A/D	analog-to-digital
ADU	ammonium diuranate
ATR	advanced test reactor
AVR	German pebble-bed reactor
AWCC	active well coincidence counter
BCD	binary coded decimal
BPHA	benzoylphenylhydroxylamine
BTFA	benzoyltrifluoroacetone
BWR	boiling water reactor
CPC	controlled-potential coulometer
CRT	cathode ray tube
DOE	U.S. Department of Energy
DTPA	diethylenetriamine pentaacetic acid
DUEGG	dual energy gamma gauge
EDTA	ethylenedinitrilo tetraacetic acid
FBR	fast breeder reactor
FFTF	fast flux test facility
FWHM	full width half maximum
GAE	general analytical evaluation
GAMAS	General Atomic material assay system
HEPA	high-efficiency particulate air
HLNCC	high-level neutron coincidence counter
hpGe	high-purity germanium
HTGR	high-temperature gas reactor
HTR	high-temperature reactor
HEU	highly enriched uranium
IAEA	International Atomic Energy Agency
IDMS	isotope dilution mass spectrometry
ISAF	isotopic source adjustable fissometer
ISAS	isotopic source assay system
LEU	low enriched uranium
LINAC	linear accelerator
LWBR	light water breeder reactor
LWR	light water reactor
MCA	multichannel analyzer
MC&A	material control and accounting
MECAS	multienergy californium assay system

MEGAS	multienergy gamma assay system
MIBK	methyl isobutyl ketone
MONAL	mobile nondestructive assay laboratory
MOX	mixed oxide fuel (uranium and plutonium)
MTR	materials testing reactor
NBL	New Brunswick Laboratory
NBS	National Bureau of Standards
NDA	nondestructive assay
NMS	national measurement system
NRC	Nuclear Regulatory Commission
NWCC	neutron well coincidence counter
PADAP	2-(2-pyridylazo)-5-diethylaminophenol
PAN	1-(2-pyridylazo)-2-naphthol
PAPAS	pin and pellet assay system
PAR	4-(2-pyridylazo)resorcinol
PBF	power burst facility
PHA	pulse-height analyzer
PM	photomultiplier
PMT	photomultiplier tube
PVC	polyvinyl chloride
PWR	pressurized water reactor
RD	Random Driver
RE	rare earth
RMS	root mean square
RSD	relative standard deviation
SALE	safeguards analytical laboratory evaluation
SAM	stabilized assay meter
SCA	single-channel analyzer
SCE	saturated calomel electrode
SGS	segmented gamma scanner
SNAP	shielded neutron assay probe
SNM	special nuclear material
SPERT	special power excursion reactor tests
SRM	standard reference material
SSAS	small sample assay system
TBP	tributyl phosphate
TDR	time domain reflectometry
TOPO	tri-m-octylphosphine oxide
TRIGA	training reactor, isotopes production, General Atomic
TTA	thenoyltrifluoroacetone
UNH	uranyl nitrate hexahydrate
WEP	water-extended polyester
XRF	X-ray fluorescence
ZPPR	zero power plutonium reactor
ZPR	zero power reactor

CHAPTER 1

Introduction

1.1 MEASUREMENTS AND NUCLEAR SAFEGUARDS

Manufacturers licensed to process and use special nuclear material (SNM: uranium-235, uranium-233, and plutonium) have a legal and ethical responsiblity to prevent and/or detect the diversion of these nuclear materials by anyone for any unauthorized use. Nuclear safeguards systems used by licensees to protect SNM include both physical security and material control and accounting (MC&A) systems.

Physical security systems are designed to prevent and/or detect unauthorized movement or removal of SNM from the plant site or from controlled areas within the plant. Physical security includes qualitative detection measurements, physical barriers, surveillance, and enforced work rules and procedures.

Material control and accounting systems are designed to detect losses of SNM from the process, and are based on quantitative measurements that are used to form material balances within the process. Accordingly, the ability of measured material balances to detect significant losses from the process depends greatly on measurement errors. The selection and proper application of adequate measurement methods for each of material forms in the fuel cycle are essential for licensees to meet loss detection limits required by Federal regulations.

1.2 PURPOSE AND SCOPE OF THIS HANDBOOK

This handbook is intended primarily to provide reliable information on the applications, capability, and performance of measurement methods for use by the Nuclear Regulatory Commission (NRC) and the licensees. It is designed to serve as one basis for the NRC staff to—

(1) Issue regulatory guides
(2) Evaluate MC&A plans submitted by licensees
(3) Evaluate the performance of MC&A systems in place
(4) Initiate research and development work

The licensees and other processors can use the handbook as a basis for—

(1) Selecting methods for designing and upgrading MC&A systems to meet Federal regulations

(2) Evaluating the performance of methods in use
(3) Initiating research and development work

The scope of this handbook includes applicable bulk measurements, chemical assay, passive nondestructive assay (NDA), and active NDA methods for all uranium- and plutonium-bearing materials routinely encountered in U.S. nuclear facilities, including feed and source materials, intermediate and final products, recycled materials, inventory materials, scrap and waste, measured discards, and process equipment holdup material.

The information presented is mostly concerned with specific applications and performance of measurement methods, the factors that impact performance, and other considerations related to method selection or evaluation. Detailed experimental procedures are not presented, but literature references are cited to guide the user to studies and procedures for implementation of the methods selected.

Measurement information and data were gathered from the literature, from a survey of production facilities, and from a survey of exchange programs. A number of NRC licensee and DOE production facilities were visited to obtain applications and performance data on methods currently being used in routine production operations. These data represent the state of the practice and are considered the most reliable estimates of expected performance. Each of the methods surveyed at the facilities was operated under an established measurement control system and was actually being used in routine production operations for safeguards purposes. In contrast, much of the literature data were collected under research and development conditions; therefore, the performance data may not represent routine operations. The survey of exchange programs included the Safeguard Analytical Laboratory Evaluation (SALE), the General Analytical Evaluation (GAE), the Plutonium Metal Exchange, and the Uranium Metal Exchange. The conditions under which these performance data were collected are not well defined. Some participants performed the measurements under research and development conditions, some under routine conditions, and some used the exchange program as a training exercise for analysts. The data from these three surveys have not been combined, but are reported and discussed separately.

1.3 ORGANIZATION AND USE OF THIS HANDBOOK

This handbook is organized to be used as a reference book. Chapter 2 is a tabular summary of applications, methods, and performance, and is designed to provide rapid reference to method performance and a preliminary screening of appropriate methods for specific applications based only on performance (random and systematic error). The tables in

Chapter 2 list each application, the appropriate methods available, and the performance of the methods for that application. The source of the performance data is designated by L (literature survey), U (users survey), or E (exchange program survey). Applications similar to the material to be measured can be located and methods suitable to meet performance requirements can be selected. The cross-reference numbers in the last column refer the reader to the appropriate sections in Chapter 3 through 6 for more detailed information.

Chapters 3 through 6 describe bulk measurement, chemical assay, passive NDA, and active NDA methods, respectively. The information presented for each method is organized into 10 subsections. The subsections and the general scope of information to be found are as follows:

(1) Description of Method
  - Brief discussion of basic principles
  - Summary of methodology and procedure

(2) Scope of Applications
  - Material type
  - Chemical/physical form
  - Conditions for use
  - Limitations on use

(3) Summary of Performance
  - Applications
  - Special conditions
  - Random error
  - Systematic error
  - Accuracy
  - Bias

(4) Equipment
  - Special instruments and apparatus required
  - Approximate cost
  - Special requirements of instruments and apparatus

(5) Major Sources of Error
  - Major factors affecting performance

(6) Measurement Control Requirements
  - Standards, reference materials, and traceability to national measurement system
  - Calibration frequency and method
  - Calibration verification frequency and method
  - Form of calibration curve and method of data fitting

(7) Data Analysis Requirements
  - Measurement computation requirements
  - Measurement control computation requirements
  - Hardware and software requirements

(8) Survey of Selected Literature
    - Description of specific applications
    - Discussion of performance

(9) Survey of Production Facilities
    - Description of specific applications
    - Discussion of performance

(10) Survey of Exchange Programs
    - Applications
    - Summary of performance

Using this additional information, a final selection of methods to be used in an MC&A system can be made. Information gathered from the cited references can be used to implement the measurement methods selected.

CHAPTER 2

Summary of Applications, Methods, and Performance

2.1 INTRODUCTION

2.1.1 Method Screening

The tables of applications, methods, and performance presented in this chapter are intended to provide the primary basis for screening the methods available for specific applications. They are also intended to provide a quick reference to expected method performance for specific material or sample types.

The most important criteria for selecting a method to measure a specific sample or material type are the following:

(1) What methods have been used to make the measurement on this type of sample or material?

(2) Of the applicable methods, which yield results consistent with the needs of the material control and accounting (MC&A) system?

With these tables the user can further evaluate the candidate methods he has identified by referring to the more detailed information presented in Chapters 3 through 6 of this handbook.

2.1.2 Information Sources

The applications and performance information and data were collected from surveys of the users, the literature, and the exchange programs. Data from these three sources are not combined but are identified separately in the tables because each may represent information generated under different conditions or for different goals. Care was taken during the users' survey to collect data only on methods used under routine production conditions with regard to material types, analyst training and education, sample load, measurement controls, and statistical evaluation. The conditions and goals under which the literature and exchange program data were generated are not as well defined. Therefore, the applicability of these performance data to routine production conditions is less certain.

2.1.3 Design of the Tables

The tables are divided into four major columns: applications, method, performance, and cross references to other sections of the handbook. The applications column presents the most characteristic attributes of the material/sample to be measured. The method column lists the methods that have been used for that application. The performance column lists the relative random and systematic errors (when available) for each application and method combination. The cross reference column identifies the source of information: literature survey, users' survey, exchange program survey, and refers the reader to the appropriate section of the handbook for more detailed information.

2.1.4 Definitions of Performance Terms

2.1.4.1 Random Error

The random errors presented in the tables are relative standard deviations (RSDs) for a single determination. The random errors were estimated from replicate measurements, mostly on samples but sometimes on standards.

2.1.4.2 Systematic Error

In most cases the systematic errors reported in this handbook refer to calibration error. Systematic error is usually estimated from 15 replicate calibration measurements using traceable standards. It is a statistical combination of the standard deviation of the mean determined during calibration and the total uncertainty associated with the stated value of the traceable standard.

2.1.4.3 Bias

For data presented in this handbook, it is assumed that sample measurements are corrected for known biases estimated during calibration. When bias values are presented in the tables, they refer to the bias observed between two bias-corrected methods and may be viewed loosely as systematic errors.

2.1.4.4 Accuracy

In several instances, particularly for data obtained from the literature, accuracy values are reported. Accuracy is a vague term subject to many definitions. In most cases, the authors reporting accuracy may have intended to express the total error of a single determination including random and systematic errors, but there is no assurance of this.

2.2 SUMMARY OF BULK MEASUREMENT METHODS

2.2.1 Weight Measurements of Uranium- and Plutonium-Bearing Materials (Table 2.1)

In these tables the applications are ordered in object weight increments with the types of weighing devices, their capacities, and readability grouped under each application range. In general, the lower object weight relates to the higher error when a range is presented in the performance column of the table.

The weighing device with a maximum capacity slightly greater than the object weight and the smallest readability increment will usually yield the best performance.

2.2.2 Volume Measurements of Uranium and Plutonium Solutions (Table 2.2)

Unlike weight measurements, volume measurements based on liquid level determination depend on the design of the vessel containing the solutions. For a given tank capacity, small diameter tanks enable more accurate volume measurements than large diameter tanks, regardless of the method used for liquid level measurement. When Raschig rings are added to tanks for criticality protection, volume measurements are usually degraded.

The applications are ordered according to volume increments. The volume measurement methods applicable to a given volume increment are grouped according to the solution being measured and tank characteristics, when known. When a range of performance data is presented, the smaller error usually applies to the upper bound of the volume increment.

2.2.3 Flow Measurements of Process Streams (Table 2.3)

Although flow measurements are routinely used in nuclear plants for process control, these measurements are only rarely used for MC&A purposes. As a result, performance data on these techniques are sparse and may not be directly related to measurements taken in radioactive operations. The data presented are intended to give a rough indication of the performance that might be achieved with adequate measurement control procedures. Flow measurements might provide real-time bulk measurement on flow streams that cannot presently be evaluated by other bulk measurement methods.

2.3 SUMMARY OF URANIUM MEASUREMENT METHODS

2.3.1 Inhomogeneity of Uranium-Bearing Materials (Tables 2.4 and 2.5)

The purpose of the inhomogeneity data is to demonstrate the potential impact of elemental and isotopic inhomogeneity and sampling of uranium-bearing materials on the performance of uranium assay methods. In some cases sampling error can dominate the total error of an assay regardless of which assay method is used.

Some of the sampling error data (footnoted) were estimated from the random error of sample measurements and the random error of standard material measurements during calibration. The other data were determined by replicate sampling and analysis.

Sampling methods should be carefully chosen to reduce sampling error when the material is inhomogeneous. Some materials such as waste and scrap materials tend to be very inhomogeneous and therefore may require more advanced sampling methods to reduce error to acceptable limits. Product and feed materials tend to be more homogeneous, thus simpler sampling methods might be satisfactory.

2.3.2 Uranium Assay of Feed and Product Material (Table 2.6)

Feed, product, and intermediate products are generally well-defined, homogeneous materials relatively free from impurities. In the application section of Table 2.6 the materials are arranged in the following order:

(1) Uranium metal, alloys
(2) Uranium hexafluoride (UF_6)
(3) Uranium tetrafluoride (UF_4)
(4) Uranium oxide (U_3O_8)
(5) Uranium dioxide (UO_2)
(6) Uranium carbide
(7) Uranyl nitrate crystals
(8) Uranium solutions
(9) Uranium/thorium oxides
(10) Uranium/thorium carbides
(11) Uranium/thorium solutions
(12) Uranium/plutonium oxides
(13) Uranium/plutonium carbides
(14) Uranium/plutonium solutions
(15) Fuel rods, plates, elements
(16) Spent fuel rods

To evaluate errors for the total amount of uranium, the errors for chemical assay must be combined with bulk measurement errors and sampling errors. The chemical assay errors that are definitely known to include sampling errors are identified in the tables.

For nondestructive assay (NDA) methods, the random and systematic errors presented are dependent to some extent on several factors including counting time, detector, matrix, and geometry. Therefore, in some cases, ranges of errors may refer to a range of variations in these factors. A more detailed breakdown of factors and performance is presented in Chapters 5 and 6.

2.3.3 Uranium Assay of Solid Scrap and Waste Materials (Table 2.7)

Scrap and waste are poorly defined materials that may be recycled, processed for volume reduction, recovered, or discarded. Generally, high concentration scrap is assumed to be recoverable, and low concentration waste is discarded; however, this compilation makes no such judgments. The applications are arranged generally in decreasing concentrations in the following order:

(1) Clean scrap—high concentration
(2) Miscellaneous scrap—high concentration
(3) Dirty scrap—high concentration
(4) Dirty scrap/waste
(5) Dirty scrap/waste—low concentration

The random error of chemical assay methods may or may not include sampling error. Performance data known to include sampling error are identified. Bulk, sampling, and analytical errors must be combined to estimate total error in the amount of uranium. The range of performance of NDA methods in some cases may cover a range of experimental conditions. See Chapters 5 and 6 for a breakdown of the performance data as a function of experimental factors.

2.3.4 Uranium Assay of Waste Solutions (Table 2.8)

Uranium waste solutions include solutions that are impure or dilute or both. These solutions may be processed to recover the uranium or processed through waste treatment facilities and discarded.

2.3.5 Measurement of Uranium Holdup in Process Equipment (Table 2.9)

Holdup is defined as the uranium remaining in the process equipment of facilities after a process line or facility has been drained of in-process material, stored items, and containers or after the equipment has been cleaned. Because of the complexity and difficulty of such measurements, little information is available from the users' survey or in the literature. This measurement area requires much additional research and development.

2.3.6 Uranium Isotopic Analysis (Table 2.10)

The isotopic analysis of uranium-bearing materials usually refers to the percent of ^{235}U relative to total elemental uranium (^{235}U enrichment). The applications are arranged in the following order:

(1) Uranium metal, alloys
(2) Uranium hexafluoride (UF_6)
(3) Uranium tetrafluoride (UF_4)
(4) Uranium oxide (U_3O_8)
(5) Uranium dioxide (UO_2)
(6) Uranium carbide
(7) Uranium solutions
(8) Uranium/plutonium oxide
(9) Uranium/plutonium carbides
(10) Scrap

2.4 SUMMARY OF PLUTONIUM MEASUREMENT METHODS

2.4.1 Inhomogeneity of Plutonium-Bearing Materials

Although no inhomogeneity data were collected on plutonium-bearing materials, it might be expected that sampling problems for plutonium would be similar to those presented for uranium in Tables 2.4 and 2.5. For example, feed and product materials would be expected to be quite homogeneous, presenting fewer sampling problems, while scrap and waste materials would be more inhomogeneous, requiring more advanced sampling methods.

2.4.2 Plutonium Assay of Feed and Product Materials (Table 2.11)

Feed and product materials are generally well-defined, homogeneous materials having few impurities. The applications are arranged in the following order:

(1) Plutonium metal, alloys
(2) Plutonium fluoride
(3) Plutonium green cake
(4) Plutonium dioxide (PuO_2)
(5) Plutonium solutions
(6) Plutonium/thorium carbide pellets
(7) Plutonium/uranium metal alloy
(8) Plutonium/uranium oxides
(9) Plutonium/uranium carbides
(10) Plutonium/uranium solutions
(11) Fuel rods
(12) Spent fuel rods and solutions

To evaluate the measurement error for the total amount of plutonium, the error for chemical assay must be combined with bulk measurement and sampling errors. The chemical assay errors that are definitely known to include sampling error are identified in the tables.

The performance of NDA methods depends on a number of experimental factors. The range of performance presented in this table may in some cases include a range of these factors. Refer to Chapters 5 and 6 for a more detailed breakdown of performance information.

2.4.3 Plutonium Assay of Scrap and Waste Materials (Table 2.12)

Waste and scrap from plutonium processing is poorly defined, usually impure material that will be recovered, recycled, or discarded. The applications in Table 2.12 are arranged generally in the order of decreasing plutonium concentrations:

(1) Dirty scrap—high concentration
(2) Dirty scrap/waste
(3) Dirty scrap/waste—low concentration

The NDA method performance ranges may cover a range of experimental factors. See Chapters 5 and 6 for more details.

2.4.4 Measurement of Plutonium Holdup in Process Equipment (Table 2.13)

Holdup is defined as the material remaining in process lines, equipment, and facilities after all in-process material, in-line inventory, and stored material have been removed and the process lines have been cleaned. Very little application and performance data are available; much additional research and development work is needed in this area.

2.4.5 Plutonium Isotopic Analysis (Table 2.14)

Plutonium isotopic analysis refers to the determination of the isotopic abundance of one or more plutonium isotopes relative to total elemental plutonium. It can also refer to the ratio of the abundance of two isotopes; e.g., $^{239}Pu/^{241}Pu$.

The applications in this table are arranged in the following order:

(1) Plutonium metal, alloys
(2) Plutonium dioxide (PuO_2)
(3) Plutonium solutions
(4) Plutonium/uranium oxides
(5) Irradiated fuel

Table 2.1 Weight measurements on uranium- and plutonium-bearing materials

Application (Object Weight)	Method (Weigher Capacity/Readability)	Performance (% RSD)		Cross Reference	
		Random Error	Systematic Error	Source[a]	Handbook Page
0.1- to 1-kg weight range:					
0.1 to 1.0	Mechanical top loader (1.2 kg/0.01 g)	0.0045 to 0.00045	0.003 to 0.00031	U	77
0.1 to 0.2	Electronic top loader (1.2 kg/0.01 g)	0.0060 to 0.008	0.0090 to 0.005	U	92
0.5	Mechanical top loader (3 kg/0.1 g)	0.011	0.0024	U	77
0.5	Mechanical top loader (5 kg/0.1 g)	0.036	0.018	U	77
0.7	Electronic top loader (5 kg/1 g)	0.082	0.045	U	92
0.2	Mechanical top loader (10 kg/1 g)	0.23	0.16	U	77
0.1 to 0.2	Electronic load cell (10 kg/1 g)	0.45 to 0.41	0.32 to 0.18	U	92
0.5	Mechanical top loader (13 kg/1 g)	0.19	0.058	U	77
0.2	Triple beam (20 kg/1 g)	0.23	0.16	U	77
0.5	Electronic load cell (50 kg/5 g)	0.29	0.29	U	92
1- to 5-kg weight range:					
1.0 to 1.2	Mechanical top loader (1.2 kg/0.01 g)	0.00045 to 0.00038	0.00031 to 0.00026	U	77

Note—See footnote at end of table.

Table 2.1 Weight measurements on uranium- and plutonium-bearing materials (Cont'd)

Application (Object Weight)	Method (Weigher Capacity/Readability)	Performance (% RSD)		Cross Reference	
		Random Error	Systematic Error	Source[a]	Handbook Page
2.5	Mechanical top loader (3 kg/0.1 g)	0.0021	0.0012	U	77
3.0	Mechanical top loader (5 kg/0.1 g)	0.0033	0.0012	U	77
2.6	Electronic load cell (5 kg/0.1 g)	0.0029	—	U	92
2.1 to 5	Electronic load cell (5 kg/0.5 g)	0.0071 to 0.0045	—	U	92
1.3 to 4.4	Mechanical top loader (5 kg/1 g)	0.017 to 0.023	0.022 to 0.0085	U	77
2.4 to 4.4	Electronic load cell (5 kg/1 g)	0.029 to 0.015	0.014 to 0.0073	U	92
1 to 5	Mechanical top loader (6 kg/1 g)	0.05 to 0.01	0.031 to 0.01	U	77
2.5	Electronic top loader (10 kg/0.1 g)	0.0011	—	U	92
2 to 5	Mechanical top loader (10 kg/1 g)	0.043 to 0.013	0.016 to 0.0065	U	77
2 to 5	Electronic top loader (10 kg/1 g)	0.088 to 0.037	0.027 to 0.011	U	92
1 to 3.5	Mechanical top loader (13 kg/1 g)	0.094 to 0.019	0.029 to 0.0082	U	77
3 to 5	Electronic load cell (50 kg/5 g)	0.10 to 0.041	0.025 to 0.030	U	92

Note—See footnote at end of table.

Table 2.1 Weight measurements on uranium- and plutonium-bearing materials (Cont'd)

Application (Object Weight)	Method (Weigher Capacity/Readability)	Performance (% RSD)		Cross Reference	
		Random Error	Systematic Error	Source[a]	Handbook Page
5- to 10-kg weight range:					
7.3 to 10	Electronic load cell (10 kg/1 g)	0.015	0.0049	U	92
5 to 10	Triple beam (10 kg/1 g)	0.013	0.0065 to 0.0042	U	77
7 to 10	Mechanical top loader (13 kg/1 g)	0.013 to 0.0094	0.0041 to 0.0022	U	77
10	Electronic load cell (50 kg/5 g)	0.021	0.015	U	92
10	Electronic load cell (100 kg/5 g)	0.045	0.018	U	92
10- to 50-kg weight range:					
15	Large mechanical scale (20 kg/10 g)	0.053	0.023	U	77
24	Large mechanical scale (32 kg/28 g)	0.12	0.067	U	77
30	Large mechanical scale (45 kg/25 g)	0.048	0.027	U	77
10 to 41	Electronic load cell (50 kg/5 g)	0.021 to 0.014	0.015 to 0.0050	U	92
13	Beam and pendulum (50 kg/5 g)	0.017	—	U	77
15 to 40	Electronic load cell (40 kg/10 g)	0.028 to 0.208	0.019	U/L	92

Note—See footnote at end of table.

Table 2.1 Weight measurements on uranium- and plutonium-bearing materials (Cont'd)

Application (Object Weight)	Method (Weigher Capacity/Readability)	Performance (% RSD)		Cross Reference	
		Random Error	Systematic Error	Source*	Handbook Page
23 to 50	Beam and pendulum (75 kg/25 g)	0.056 to 0.025	0.035 to 0.016	U	77
10 to 26	Electronic load cell (100 kg/5 g)	0.045 to 0.028	0.018 to 0.0065	U	92
50	Beam and pendulum (150 kg/5 g)	0.012	0.0043	U	77
20 to 30	Beam and pendulum (1145 kg/0.1 kg)	0.15 to 0.10	0.15 to 0.10	U	77
50- to 100-kg weight range:					
55	Beam and pendulum (57 kg/25 g)	0.029	0.015	U	77
60	Equal arm (60 kg)	0.001	0.001	U	77
		0.0003	--	L	77
69	Beam and pendulum (90 kg/25 g)	0.018	0.011	U	77
62	Electronic load cell (100 kg/5 g)	0.026	0.0069	U	92
95	Beam and pendulum (150 kg/5 g)	0.0065	0.0023	U	77
100- to 1000-kg weight range:					
360	Beam and pendulum (360 kg/0.1 kg)	0.03	0.03	L	77
580 to 700	Beam and pendulum (1145 kg/100 g)	0.019 to 0.016	0.0060 to 0.0051	U	77

Note—See footnote at end of table.

Table 2.1 Weight measurements on uranium- and plutonium-bearing materials (Cont'd)

Application (Object Weight)	Method (Weigher Capacity/Readability)	Performance (% RSD)		Cross Reference	
		Random Error	Systematic Error	Source[a]	Handbook Page
455 to 683	Beam and pendulum (4500 kg/0.45 kg)	0.057 to 0.047	0.029 to 0.019	U	77
223 to 909	Electronic load cell (4540 kg/0.9 kg)	0.19 to 0.75	0.12 to 0.034	U	92
>1000-kg weight range:					
2769	Beam and pendulum (4500 kg/0.45 kg)	0.013	0.0047	U	77
1818 to 3182	Electronic load cell (4540 kg/0.9 kg)	0.066 to 0.054	0.022 to 0.016	U	92
18,000	Beam and pendulum (18,000 kg/2.3 kg)	0.01	0.01	L	77

[a] L = literature survey; U = users' survey of production facilities.

Table 2.2 Volume measurements on uranium and plutonium solutions

Application (Volume)	Method (Readability)	Performance (% RSD)		Cross Reference	
		Random Error	Systematic Error	Source[a]	Handbook Page
<100-L volume range:					
HEU tanks, Raschig ring filled, 8 tanks (75 to 85 L)	Sight gauge (0.1 cm)	0.13 to 0.30 (Av: 0.18)	0.16 to 1.44 (Av: 0.49)	U	105
HEU tanks, 5-in. diameter, no Raschig rings, 9 tanks (12 to 22 L)	Graduated cylinder (0.1 cm)	0.029 to 0.038 (Av: 0.034)	0.09 to 0.28 (Av: 0.27)	U	105
Pu tanks, Raschig ring filled, 6 tanks (9 to 31 L)	Sight gauge (0.05 cm)	—	0.32 to 2.1 (Av: 0.97)	U	105
Pu tanks, no Raschig rings, 3 tanks (90 L)	Differential pressure gauge, manometer	0.10 to 0.22	0.50 to 0.66	U	116
Calibration tanks (water) 14 tanks (90 L)	Sight gauge or graduated cylinder (0.25 in.)	—	0.087	U	105
100- to 200-L volume range:					
HEU tanks, Raschig ring filled, 3 tanks (139 to 153 L)	Sight gauge (0.1 cm)	0.09 to 0.1 (Av: 0.091)	0.11 to 0.19 (Av: 0.14)	U	105
Pu tanks, Raschig ring filled, 7 tanks (100 to 200 L)	Sight gauge (0.05 cm)	—	0.21 to 0.80 (Av: 0.48)	U	105
200- to 300-L volume range:					

Note—See footnotes at end of table.

Table 2.2 Volume measurements on uranium and plutonium solutions (Cont'd)

Application (Volume)	Method (Readability)	Performance (% RSD)		Cross Reference	
		Random Error	Systematic Error	Source[a]	Handbook Page
Pu tanks, Raschig ring filled, 22 tanks (210 to 290 L)	Sight gauge (0.05 cm)	—	0.13 to 1.3 (Av: 0.47)	U	105
300- to 400-L volume range:					
Pu tanks, Raschig ring filled, 11 tanks (310 to 400 L)	Sight gauge (0.05 cm)	—	0.05 to 1.6 (Av: 0.56)	U	105
LEU tanks, Raschig ring filled, 3 tanks (315 to 364 L)	Sight gauge (0.25 in.)	0.83 to 2.79 (Av: 1.6)	0.34 to 1.02 (Av: 0.74)	U	105
LEU tank, Raschig ring filled, 1 tank (315 L)	Sight gauge (0.12 in.)	0.83	—	U	105
Miscellaneous tank, 1 tank (300 L)	Differential pressure gauge (0.001 psi)	0.015 to 0.017	0.030 to 0.056	L	116
400- to 500-L volume range:					
Pu tanks Raschig ring filled, 14 tanks (405 to 483 L)	Sight gauge (0.05 cm)	—	0.10 to 0.59 (Av: 0.32)	U	105
LEU tanks, Raschig ring filled, 7 tanks (403 to 494 L)	Sight gauge (0.25 in.)	1.1 to 3.5 (Av: 2.2)	0.44 to 1.3 (Av: 0.76)	U	105

Note—See footnote at end of table.

Table 2.2 Volume measurements on uranium and plutonium solutions (Cont'd)

Application (Volume)	Method (Readability)	Performance (% RSD)		Cross Reference	
		Random Error	Systematic Error	Source[a]	Handbook Page
500- to 600-L volume range:					
Pu tanks, Raschig ring filled, 9 tanks (505 to 570 L)	Sight gauge (0.05 cm)	—	0.14 to 0.46 (Av: 0.31)	U	105
LEU tanks, Raschig ring filled, 6 tanks (506 to 579 L)	Sight gauge (0.25 in.)	0.71 to 2.2 (Av: 1.4)	0.26 to 0.74 (Av: 0.53)	U	105
600- to 700-L volume range:					
Pu tanks, Raschig ring filled, 2 tanks (610 L)	Sight gauge (0.05 cm)	—	0.082 to 0.16 (Av: 0.12)	U	105
LEU tanks, Raschig ring filled, 1 tank (627 L)	Sight gauge (0.25 in.)	0.71	0.26	U	105
700- to 800-L volume range:					
Pu tanks, Raschig ring filled, 3 tanks (770 L)	Sight gauge	—	0.73	U	105
800- to 900-L volume range:					
Pu tanks, Raschig ring filled, 4 tanks (800 to 900 L)	Sight gauge (0.05 cm)	—	0.15 to 0.33 (Av: 0.25)	U	105

Note—See footnote at end of table.

Table 2.2 Volume measurements on uranium and plutonium solutions (Cont'd)

Application (Volume)	Method (Readability)	Performance (% RSD)		Cross Reference	
		Random Error	Systematic Error	Source[a]	Handbook Page
>1000-L volume range:					
Pu tanks, Raschig ring filled, 3 tanks (1550 to 2320 L)	Sight gauge (0.05 cm)	—	0.22 to 0.40 (Av: 0.30)	U	105
HEU tanks, no Raschig rings, 1 tank (5300 L)	Sight gauge (fill to mark)	—	0.83	U	105
Miscellaneous tanks, 2000 to 20,000 L	Differential pressure, water manometers	0.08 to 0.24	0.07 to 0.85	L	116
Miscellaneous tanks, 2000 to 20,000 L	Differential pressure, oil manometers (0.01 in.)	0.11 to 0.85	0.09 to 0.35	L	116
Miscellaneous tanks, 2000 L	Differential pressure, pneumatic pressure gauge	0.1 to 0.3	0.04 to 0.4	L	116
Miscellaneous tanks, 3000 L	Differential pressure, electromanometer (0.001 psi)	0.11	0.038	L	116
Miscellaneous tanks, (volume unknown)	Sight Gauges:				
	3 m (0.1 cm)	0.014	—	L	105
	1.4 m (0.1 cm)	0.1	0.05	L	105
	0.767 m (0.1 cm)	0.54	0.18	L	105
	Time domain reflectometer				
	19.3 cm	5	2.6	L	125
	2 m	0.1	—	L	125

Note—See footnote at end of table.

Table 2.2 Volume measurements on uranium and plutonium solutions (Cont'd)

Application (Volume)	Method (Readability)	Performance (% RSD)		Cross Reference	
		Random Error	Systematic Error	Source[a]	Handbook Page
Miscellaneous tanks (volume unknown) cont'd	**Chemical and/or isotopic dilution:**				
	Magnesium tracer	0.34 (accuracy)		L	131
	^{6}Li/^{7}Li	0.31 (accuracy)		L	131
	Zinc tracer	0.33 (accuracy)		L	131

HEU = highly enriched uranium; LEU = low enriched uranium.

[a] L = literature survey; U = users' survey of production facilities.

Table 2.3 Flow measurements on process streams

Application	Method	Performance: Sensitivity (% full scale)	Performance: Accuracy (%)	Cross Reference: Source[a]	Cross Reference: Handbook Page
Quantity measurement	Positive displacement meters:				
	Piston	1	0.2 to 1	L	134
	Nutating disk	1	0.2 to 1	L	134
	Rotary vane	1	0.2 to 1	L	134
	Metering pump	2	0.5 to 1	L	134
Rate measurement	Variable-head meters:				
	Orifice	2	0.5 to 2	L	134
	Venturi	2	1	L	134
	Pitot	2	1 to 3	L	134
	Variable-area meters:				
	Rotameter	2	0.5 to 2	L	134
	Piston (plugged and ported) cylinder	—	0.5 to 2	L	134
	Air lift	—	3 to 10	L	134
	Ejector	—	5 to 20	L	134
	Velocity and current meter:				
	Electromagnetic	—	1	L	134
	Turbine	0.25	0.25 to 1	L	134
	Vortex	—	0.25 to 1	L	134
	Thermal	—	2	L	134
	Ultrasonic	—	0.1 to 1	L	134

[a] L = literature survey.

Table 2.4 Inhomogeneity of uranium-bearing materials—elemental

Application	Method	Performance (% RSD)		Cross Reference	
		Type of Inhomogeneity	Random Error	Source[a]	Handbook Page
Feed, Product, Intermediate Product:					
UO_2 powder:					
87.6% U in 5-gal. metal cans (20 kg)	Mix (tumble end to end) 12 min; core sample one 50-g sample from each of 3 cans per lot, one sample per can.	Can to can	0.032[b]	U	158
88% U in 3-gal. shipping containers (25 kg)	Grab sample (scoopula) one 5-g sample per container, one container per batch.	Batch to batch	0.005[b]	U	158
88% U in 12-in. diameter by 18-in. high polylined can (29 kg)	Grab sample (scoop) 10 g from 3 in. below top center, each of 3 randomly selected cans per lot.	Can to can	0.014[b]	U	158
87% blend in 12-in. high by 10-in. diameter fiberpacks (18 kg)	Mix (roll) 10 min; core sample three 30- to 40-g samples and composite.	Pack to pack	<0.020[b]	U	158
Blend material in cans	Mix (V-cone blend) for 10 min 2 cans of a several-can blend batch, grab sample (scoop) two 50-g samples from each blended can.	Within can	<0.027[b]	U	158
UO_2 pellets:					
88% U in 100-tray lots, 900 to 1200 pellets per tray	Random selection, 1 pellet every 25 trays (4 pellets), composite, crush.	Lot to lot	<0.020[b]	U	158
88.1% U in pellet trays	Random selection of 5 pellets from last third of pellet lot.	Within lot	<0.025[b]	U	158

Note—See footnote at end of table.

Table 2.4 Inhomogeneity of uranium-bearing materials—elemental (Cont'd)

Application	Method	Performance (% RSD)		Cross Reference	
		Type of Inhomogeneity	Random Error	Source[a]	Handbook Page
88% U in 290 boat (2000 pellets per boat) lots	Random selection of 5 pellets from each third of a lot, composite and chunk each 5-pellet third.	Within lot	<0.008[b]	U	158
U_3O_8 powder: 75% subblend in 12-in. high by 10-in. diameter fiberpacks (18 kg)	Mix (roll) 10 min, core sample three 30- to 40-g samples, and composite.	Pack to pack	2.2[b]	U	158
UO_2, U_3O_8 powder: HTGR feed in 1-gal. can (3.5 kg)	Core sample a 15-g sample from each can, composite, duplicate analyses.	Lot to lot	0.01	U	158
Uranium metal: sheets, TRIGA feed	Random selection of duplicate samples from 20% of the sheets per lot.	—	<0.06[c]	U	158
(U, Th) oxide powder. HTGR material in 1/2- to 1-gal. poly bottles (≈1 kg)	*Core sample duplicate 15-g samples.*	—	0.04 *to* 0.18[c]	U	158
(U, Th) oxide, SiC coated: *HTGR* material in 1/2- to 1-gal. poly bottles (≈1 kg)	*Core sample duplicate 15-g samples.*	—	*0.4*[c]	U	158
(*U, Th*) carbide particles: 100- to 300-µm size in 8- to 9-kg metal bottles	*Split (10-way splitter) duplicate 15-g* samples from each of 2 bottles every 10 bottles.	—	*0.03 (300 µm)*[c] 0.19 (100 µm)[c]	U	158
(U,Th) carbide, SiC coated 100- to 400-µm particles in 1-gal. metal cans (3.6 kg)	Mix, Hobec proportional rotary stream splitter (1/10), collecting 30 g, split (riffle) to duplicate 15-g samples	—	0.40 (100 µm)[c] 1.3 (300 µm)[c]	U	158

Note—See footnote at end of table.

Table 2.4 Inhomogeneity of uranium-bearing materials—elemental (Cont'd)

Application	Method	Performance (% RSD)		Cross Reference	
		Type of Inhomogeneity	Random Error	Source[a]	Handbook Page
U-Zr alloy, hydride:					
Powder (TRIGA fines) in 1/2- to 1-gal. poly bottles (1 kg)	Core sample three 5-g samples and composite.	—	2.4[c]	U	158
Short rods (TRIGA meats), 0.5- to 1.5-in. diameter by 5- to 5.5-in. long	Random selection of 2 rods (large meats) or 3 rods (small meats), machine 1 to 2 g from each end of each rod.	—	0.65[c]	U	158
Uranyl nitrate solutions in cylindrical 300-gal. tank with Raschig rings	Mix (circulate), petcock sample (tap in circulate line) 10- to 20-mL sample, remix, withdraw second sample.	Within tank	0.22[b]	U	158
HEU dissolver solutions in critical safe tanks, 5-in. diameter, 6-ft. high	Mix (circulate between tanks) 20 min, withdraw (spigot at pump outlet) 10-mL sample, remix 5 min, withdraw second sample.	Within tank	0.86[b]	U	158
Scrap:					
Clean scrap: homogeneous UO_2 powder with $(NH_4)_2C_2O_4$ and NH_4HCO_3	Mix (mechanical blend), grab sample duplicate samples, duplicate analyses per sample.	Within container	0.33	U	158
Dirty scrap:					
UO_2/U_3O_8 powder in 5-gal. metal cans (20 to 35 kg)	Mix (tumble) 12 min, grab sample (scoopula) replicate 40- to 50-g samples from top center, replicate analyses per sample	Within can	3.7	U	158

Note—See footnote at end of table.

Table 2.4 Inhomogeneity of uranium-bearing materials—elemental (Cont'd)

Application	Method	Performance (% RSD)		Cross Reference	
		Type of Inhomogeneity	Random Error	Source[a]	Handbook Page
Inhomogeneous UO_2 powder, Gd_2O_3, NH_4HCO_3, $(NH_4)_2C_2O_4$, and hard scrap	Grab sample duplicate samples, duplicate analyses per sample.	Within container	0.6	U	158
Sludge, sweepings, ash, filter knockdown (30% to 79% U) in 2- to 5-gal. polylined fiberpacks (15 kg)	Core sample, four 50-g samples per container; sample only certain proportion of the containers in a specific material category.	Within container	6.4 (0.8 to 23)	U	158
Calcined material (30% U) in calciner boats	Grab sample (scoop) two 10-g samples from surface.	Within batch	9.1[b]	U	158
Incinerator ash (30% U) in 2-L poly bottle	Mix (ball mill) 30 min, grab sample two 10-g samples from ball-mill dump stream (into bottle).	Within bottle	24[b]	U	158
Ash (≈31% U) in 18-in. high by 10-in. diameter cans (12 kg)	Grab sample (scoop) a 50-g sample from top quarter of can.	Can to can	13[b]	U	158
Grinder sludge in 5-gal. plastic bucket (18 kg)	Mix (stir with scoopula), grab sample (scoopula) replicate 20- to 25-mL samples top center, replicate analyses per sample.	Within can	3.5	U	158
ADU (wet, clay-type) in 5-gal. plastic bucket (18 kg)	Mix (stir with scoopula), grab sample (scoopula) replicate 20- to 25-mL samples, top center, replicate analyses per sample.	Within can	12	U	158

Note—See footnote at end of table.

Table 2.4 Inhomogeneity of uranium-bearing materials—elemental (Cont'd)

Application	Method	Performance (% RSD)		Cross Reference	
		Type of Inhomogeneity	Random Error	Source[a]	Handbook Page
(U-Zr) oxide, very fine powder (TRIGA solids/sludges) in 2-L poly bottles	Mix (roll mill) 15 min, core sample duplicate 5-g samples.	—	2.4[c]	U	158
Raffinate solution in 300-gal. cylindrical tank with Raschig rings	Mix (circulate), petcock sample (tap in circulate line) 10- to 20-mL sample, remix, withdrew second sample.	Within tank	0.62[b]	U	158

HTGR = high-temperature gas reactor; TRIGA = training research isotope General Atomic.

[a] U = users' survey of production facilities.

[b] Estimated (see Section 4.3).

[c] Error calculation method not defined.

Table 2.5 Inhomogeneity of uranium-bearing materials—isotopic

		Performance (% RSD)		Cross Reference	
Application	Method	Type of Inhomogeneity	Random Error	Source[a]	Handbook Page
UO_2 powder: Blend material (LEU) in 12-in. high by 10-in. diameter fiberpacks (18 kg)	Mix (stratify), grab sample (1-g spoon) one 1-g sample from each of 4 fiberpacks (different levels).	Pack to pack	0.24[b]	U	158
UO_2 pellets: LEU material in 100 tray lots, 900 to 1200 pellets per tray	Random selection of one pellet every 25 trays, composite, crush.	Lot to lot	0.39[b]	U	158
UO_2 powder and pellets, pure and scrap (LEU) in multilot projects of varying enrichments	Grab sample, 1 sample per lot for pure powder, 2 samples per lot for pellets, 3 samples per lot for scrap powder	Lot to lot	0.31	U	158
Ash (LEU) in 18-in. high by 10-in. diameter can (12 kg)	Grab sample (scoop) one 50-g sample from top half of each can.	Can to can	1.9[b]	U	158

[a] U = users' survey of production facilities.

[b] Estimated (see Section 4.3).

Table 2.6 Uranium Assay of Feed and Product Materials

Application	Method	Performance (% RSD)		Cross Reference	
		Random Error	Systematic Error	Source[a]	Handbook Page
Uranium metal, alloys:					
Metal	Titrimetric: Davies and Gray/NBL	"No bias"		L	201
		0.004	—	E	201
	Titrimetric: Jones reduction, excess Cr(VI), back titrate with Fe(II), potentiometric end point	0.031	—	U	216
		0.007	—	E	216
	Titrimetric: Ti(III) reduction, Fe(III) oxidation, titrate the Fe(II) formed with Ce(IV), potentiometric end point	0.002	—	E	216
Metal, NBS-960 standard	Titrimetric: Davies and Gray/NBL	0.05	0.018	U	201
	Controlled-potential coulometry	0.15	0.039	U	230
	X-ray fluorescence	0.33[b]	0.085	U	366
Metal particles, TRIGA feed	Titrimetric: Davies and Gray/NBL	0.06[b]	0.017	U	201
Metal buttons, HEU, 0.5 to 4 kg ^{235}U per sample	Active well coincidence counter	0.5 to 3.2	—	L	685
Alloy material	Titrimetric: Davies and Gray	<0.04 (bias)		L	201
Zircaloy base alloy, 3% to 10% U	Titrimetric: Jones reduction, Ce(IV) titration, ferroin visual end point	0.25	—	L	216
U alloy standard material	Titrimetric: Jones reduction, Ce(IV) titration, ferroin visual end point	0.16	0.049	U	216
U alloy process material	Titrimetric: Jones reduction, Ce(IV) titration, ferroin visual end point	0.43[b]	0.049	U	216

Note—See footnote at end of table.

Table 2.6 Uranium Assay of Feed and Product Materials (Cont'd)

Application	Method	Performance (% RSD)		Cross Reference	
		Random Error	Systematic Error	Source[a]	Handbook Page
TRIGA alloy standard material	Titrimetric: Davies and Gray/NBL	0.06	0.018	U	201
TRIGA alloy process material	Titrimetric: Davies and Gray/NBL	0.63[b]	0.018	U	201
Alloy, UAl$_x$ powder, HEU, 1-gal. can, 90 cans per lot, 320 kg lot	Delayed neutrons: 14 MeV neutrons	0.2 ± 0.95 (accuracy for lot total)		L	632
Alloy, UAl$_x$ powder, HEU, 1-gal. can, 0.5 to 4.5 kg ^{235}U per can	Photofission: linear accelerator	2.8	—	L	700
^{235}U plates, HEU	Photoneutron: linear accelerator	1 to 10 (accuracy)		L	705
Uranium hexafluoride (UF$_6$)	Gravimetric	0.08	—	L	194
		0.039[b] (0.02 to 0.062)	0.017	U	194
		0.038, 0.075	—	E	194
	Titrimetric: Davies and Gray/NBL	0.28	—	E	201
	Controlled-potential coulometry	0.044, 0.46	—	E	230
Uranium tetrafluoride (UF$_4$):	Gravimetric	0.02	—	L	194
		0.058	—	U	194
Uranium oxide (U$_3$O$_8$): Powder, standard material	Titrimetric: Jones reduction, excess Cr(VI), back titrate with Fe(II), potentiometric end point	0.006	—	L	216
		0.049	—	U	216
	Titrimetric: lead reduction, Fe(III) oxidation, titrate Fe(II) formed with Cr(VI)	0.03	—	L	216

Note—See footnote at end of table.

Table 2.6 Uranium Assay of Feed and Product Materials (Cont'd)

Application	Method	Performance (% RSD)		Cross Reference	
		Random Error	Systematic Error	Source[a]	Handbook Page
	Titrimetric: Cr(II) reduction, Cr(VI) titration, potentiometric end point	0.085	0.033	U	216
	Titrimetric: Davies and Gray/NBL	0.091, 0.12	0.034, 0.040	U	201
	Titrimetric: Davies and Gray, visual	0.12 (0.048 to 0.20)	0.032	U	201
Powder, HEU, 0.25 to 2 kg ^{235}U per can	Active Well Coincidence Counter	6 to 0.5	—	L	685
Powder, 3 kg U_3O_8	Delayed neutron: Van de Graaff	2.6 (accuracy)		L	636
Uranium dioxide (UO_2):					
Powder, pure, product and standard material	Gravimetric	0.024[b] (0.008 to 0.059,	0.014 (0.001 to 0.023)	U	194
		0.017 (0.004 to 0.053)	—	E	194
	Titrimetric: Davies and Gray/ NBL	0.11	0.035	U	201
		0.065 (0.004 to 0.11)	—	E	201
	Titrimetric: Davies and Gray, visual	0.078, 0.56	—	E	201
		0.26[b]	0.034	U	201
	Controlled-potential coulometry	0.080[b]	0.039	U	230
		0.066	—	E	230
	Titrimetric: Jones reduction, Cr(VI) titration, visual end point, or back titrate excess Cr(VI) with Fe(II) to potentiometric end point	0.021	—	E	216
	Titrimetric: Jones reduction, Ce(IV) titration, ferroin visual end point	0.015, 0.70	—	E	216

Note—See footnote at end of table.

Table 2.6 Uranium Assay of Feed and Product Materials (Cont'd)

Application	Method	Performance (% RSD)		Cross Reference	
		Random Error	Systematic Error	Source[a]	Handbook Page
	X-ray fluorescence: internal standard	0.15	—	*E*	368
Powder, 9.3 g ^{235}U per can	Subthreshold: isotopic photoneutron source	1.3	<1 (estimated)	L	650
Powder, LEU, 2.7 to 3.8 kg U per can	Photofission: linear accelerator	1.8	—	L	700
Powder or pellets, contains ZrO_2, 1.4 to 3.6g U per sample	Delayed neutron: 14 MeV	1.3 (accuracy)		L	632
Powder, HEU, 1-qt can	Isotopic Source Assay System	2.0 (accuracy)		L	665
Powder, polyethylene vials	Small Sample Assay System	0.4	—	L	696
HTGR feed: U_3O_8 powder, UO_2 powder, $(U,Th)O_2$ powder	Titrimetric: Davies and Gray/NBL	0.89[b]	0.017	U	201
PBF fuel powder in ½-gal. cans, ≈600 g ^{235}U per can	Isotopic Source Assay System	1.5 (accuracy)		L	665
BWR fuel (mockup)	Delayed neutron: Van de Graaff	6 (accuracy)		L	638
LEU and HEU inventory samples, 5 to 500 mg ^{235}U per sample	Delayed neutron: isotopic source step irradiation	2.9 (accuracy)		L	641
Verification samples, subgram to gram quantities of U per sam-	Delayed neutron: 14 MeV neutrons	3	—	L	632
Pellets: pure, product material	Gravimetric	0.011[b]	0.015	U	194
		(0.004 to 0.025) 0.007	—	E	194

Note— See footnote at end of table.

Table 2.6 Uranium Assay of Feed and Product Materials (Cont'd)

		Performance (% RSD)		Cross Reference	
Application	Method	Random Error	Systematic Error	Source^a	Handbook Page
Pellets, LEU, ½-gal. cans	Photofission: linear accelerator	2.2 (accuracy)		L	700
UO_2-stainless steel	X-ray fluorescence	0.5 to 1.0	—	L	368
UO_2-Al_2O_3	X-ray fluorescence	1.8	—	L	368
BWR fuel pellets, natural uranium	Small Sample Assay System	0.73	0.3	L	696
BWR fuel pellets, 3.3% ^{235}U enrichment	Small Sample Assay System	0.33	0.3	L	696
PBF fuel pellets in ½-gal. cans, 60 to 400 g ^{235}U per can	Isotopic Source Assay System	3.2 (accuracy)		L	665
Uranium carbide	X-ray fluorescence	0.2	—	L	368
	Titrimetric: Davies and Gray, visual	0.22^b	0.034	U	201
Uranyl nitrate crystals	Titrimetric: Cr(II) reduction, Cr(VI) titration, potentiometric end point	0.13	0.033	U	216
Uranium solutions:					
Standard solution, 20 g/L	Titrimetric: Davies and Gray/NBL	0.10^b	0.060	U	201
Standard solutions, 319g/L	Titrimetric: Davies and Gray/NBL	0.07	—	U	201
Standard solutions	Spectrophotometric: tetrapropylammonium uranyl trinitrate complex, 1 to 30 mg U	5 to 2.2	—	L	244
	Spectrophotometric: dibenzoylmethane complex	0.6	—	U	244
		2	0.51	U	244
	Spectrophotometric: peroxide complex	0.4	—	U	244

Note—See footnote at end of table.

Table 2.6 Uranium Assay of Feed and Product Materials (Cont'd)

Application	Method	Performance (% RSD)		Cross Reference	
		Random Error	Systematic Error	Source[a]	Handbook Page
Uranyl nitrate	Titrimetric: Davies and Gray/NBL	0.060 (0.009 to 0.15)	—	E	201
	Titrimetric: Davies and Gray, visual	0.14, 0.07	—	E	201
	Titrimetric: Jones reduction, Cr(VI) titration, visual end point, or back titrate excess Cr(VI) with Fe(II) to potentiometric end point	0.23, 0.078	—	E	216
	Titrimetric: Jones reduction, Ce(IV) titration, ferroin visual end point	0.11	—	E	216
	Controlled-potential coulometry, 150 to 300 mg U	0.2 to 0.1	—	L	230
	Controlled-potential coulometry, 2 to 20 mg U	0.034 to 0.20	—	E	230
	X-ray fluorescence	0.41	—	E	368
Uranyl nitrate, 50 to 500 g/L, 20-mL sample	*K*-edge absorptiometry	0.4 0.5 to 1.0 (accuracy)	—	L	457
Uranyl nitrate, sample cell, 2 to 400 mg/mL HEU	Gamma ray, NaI	1.0 (accuracy)		L	418
Uranyl nitrate, in-line monitor, 2 to 25 mg/mL HEU	Gamma ray, NaI	1.0 (accuracy)		L	418
U-Al$_x$ alloy	Controlled-potential coulometry	0.1	—	L	230
	Titrimetric: Davies & Gray/NBL	0.074[b]	0.018	U	201
U-Mo alloy	Controlled-potential coulometry	0.3 to 0.7	—	L	230
U-Nb alloy	Controlled-potential coulometry	0.1 to 0.5	—	L	230

Note—See footnote at end of table.

Table 2.6 Uranium Assay of Feed and Product Materials (Cont'd)

		Performance (% RSD)		Cross Reference	
Application	Method	Random Error	Systematic Error	Source[a]	Handbook Page
Synthetic U alloy	Controlled-potential coulometry	0.1 to 0.2	—	L	230
U-Mo-Ru alloy (95% U)	X-ray fluorescence	*0.11*[b]	0.034	U	368
Miscellaneous solutions	Titrimetric: Davies and Gray/NBL	0.07 (0.02 to 0.15)	—	L	201
	Titrimetric: Davies and Gray, high precision method	0.003 to 0.008	—	L	201
	Titrimetric: Jones reduction, Ce(IV) titration, ferroin visual end point	0.09	—	L	216
	Complexometric: EDTA, 1.2 to 27 mg U	0.5 to 0.095	—	L	225
	Complexometric: EDTA, 0.012 mg U	5.0	—	L	225
	Complexometric: EDTA, 0.1 to 100 mg U	3 to 0.3 (accuracy)		L	225
	Complexometric: DTPA, 47.2 to 953 μg U	1.3 to 0.8 (2σ error)		L	225
	Controlled-potential coulometry, 7.5 to 8 μg U	2.3	—	L	230
	Controlled-potential coulometry, 0.75 to 75 mg U	0.3 to 0.06	—	L	230
	Spectrophotometric: measurement of 416- and 426-nm lines	<5 (% error)		L	244
	Spectrophotometric: measurement of 416-nm *line only*	15 to 30 (% error)		L	244

Note—See footnote at end of table.

Table 2.6 Uranium Assay of Feed and Product Materials (Cont'd)

Application	Method	Performance (% RSD)		Cross Reference	
		Random Error	Systematic Error	Source[a]	Handbook Page
	Spectrophotometric: differential, 20 to 60 mg/mL	0.04, 0.3	—	L	244
	Spectrophotometric: uranyl carbonate complex, 0.1 to 10 mg/mL	<1%		L	244
	Spectrophotometric: dibenzoylmethane complex, 1 to 750 μg	25 to 0.57	—	L	244
	Spectrophotometric: arsenazo-III complex, 1 to 200 μg	10 to 0.36	—	L	244
	Spectrophotometric: tetrapropylammonium uranyl trinitrate complex, automated, 0.12 to 10 mg	10.4 to 0.2	—	L	244
	Spectrophotometric: benzoyl trifluoroacetone complex, 5 to 85 μg	2.9 to 0.2	—	L	244
	Spectrophotometric: 4-(2-pyridylazo) resorcinol complex, >30 μg	1	—	L	244
	X-ray fluorescence	0.4 to 5	—	L	368
Uranium/thorium oxides:	Complexometric: excess EDTA, back titrate with thorium standard to xylenol orange visual end point	<1	—	L	225
Uranium/thorium carbides:					
Beads	Titrimetric: Jones reduction, Ce(IV) titration, ferroin visual end point	0.13	—	L	216
HTGR process material	Titrimetric: Davies and Gray/NBL	0.07 to 0.28[b]	0.017	U	201
	X-ray fluorescence	0.80[b]	0.085	U	368

Note—See footnote at end of table.

Table 2.6 Uranium Assay of Feed and Product Materials (Cont'd)

Application	Method	Performance (% RSD) Random Error	Performance (% RSD) Systematic Error	Cross Reference Source[a]	Cross Reference Handbook Page
SiC coated standard material	Titrimetric: Davies and Gray/NBL	0.62	0.53	U	201
	X-ray fluorescence	0.26	1.0	U	368
SiC coated process material	Titrimetric: Davies and Gray/NBL	0.2 to 3[b]	0.53	U	201
	X-ray fluorescence	0.61[b]	1.0	U	368
HTGR coated Th/U carbide particles in 1-gal. cans	Random Driver	0.8 to 1.5	0.8 to 1.6	U	665
HTGR microspheres	Delayed neutron: Van de Graaff	0.67	—	L	638
Uranium/thorium solutions	X-ray fluorescence	1	—	L	368
Uranium/plutonium oxides:					
Powder	Titrimetric: Davies and Gray/NBL	0.17, 0.31	—	E	201
	Controlled-potential coulometry	0.095	—	E	230
	X-ray fluorescence	0.31	—	E	368
		0.4	—	L	368
	X-ray fluorescence: on-line assay	0.2, 0.5	—	L	368
Pellets	Titrimetric: Davies and Gray, visual	0.29[b]	0.034	U	201
	Controlled-potential coulometry	0.18	—	E	230
		0.27	—	L	230
LWBR fuel pellets, $^{233}UO_2/ThO_2$ pellets	Delayed neutron: isotopic source step irradiation	0.1	1.5	L	641
Uranium/plutonium carbides:					
Carbide material	Titrimetric: Davies and Gray, visual	0.45[b]	0.034	U	201
Pellets, 76% U	Controlled-potential coulometry	0.17[b]	0.039	U	230
Carbide, oxide, nitride material	Controlled-potential coulometry	0.07 to 0.15	—	L	230
$UO_2 + PuO_2 + C$, 63% U	Controlled-potential coulometry	0.39[b]	0.039	U	230

Note—See footnote at end of table.

Table 2.6 Uranium Assay of Feed and Product Materials (Cont'd)

Application	Method	Performance (% RSD)		Cross Reference	
		Random Error	Systematic Error	Source[a]	Handbook Page
Uranium/plutonium solutions:					
Purex process solution	Spectrophotometric: TTA complex, 0.2 to 1.4 mg/mL	2	—	L	244
	Spectrophotometric: thorin complex, 25 to 250 μg	2	—	L	244
Irradiated solutions	X-ray fluorescence	0.3 to 3	—	L	368
	X-ray fluorescence : automatic on-line	0.5 to 1	—	L	368
Miscellaneous solutions	Isotope dilution mass spectrometry, weight aliquots	0.15	—	L	360
	Isotope dilution mass spectrometry, volumetric aliquots	0.6 to 1.3	—	L	360
	Isotope dilution mass spectrometry, resin bead method	0.6	—	L	360
Fuel rods, plates, and elements:					
ATR fuel element	Photofission: linear accelerator	1 (accuracy)		L	700
BWR fuel rod	GE rod scanner	1.5	0.5	L	689
FBR fuel rod	FBR rod scanner	1	0.2	L	689
HTGR fuel sticks	Delayed neutron: nuclear reactor	0.3	—	L	646
	Dual Energy Gamma-ray Gauge	0.25 1.5 (accuracy)	—	L	453
	Subthreshold: isotopic photoneutron source	1	2	L	650
	Subthreshold: moderated ^{252}Cf	0.5	<1 (estimated)	L	659

Note—See footnote at end of table.

Table 2.6 Uranium Assay of Feed and Product Materials (Cont'd)

		Performance (% RSD)		Cross Reference	
Application	Method	Random Error	Systematic Error	Source[a]	Handbook Page
	Delayed neutron: isotopic source step irradiation	0.5	—	L	641
	Isotopic Source Assay System	1.2 (accuracy)		L	665
	Random Driver	1.5 (accuracy)		L	665
ATR fuel plate, 70 g ^{235}U per plate	Isotopic Source Assay System	1.5 (accuracy)		L	665
AVR fuel (U, Th, and graphite)	Subthreshold: Fermi age	1 (estimated accuracy)		L	656
LWR fuel rod	Subthreshold: Fermi age	1 (estimated accuracy)		L	656
	Commercial rod scanners	0.25 to 1 (total)		L	689
	Pin and pellet assay system	1 (total)		L	689
MTR fuel element	Delayed neutron: 14 MeV	1 (accuracy)		L	532
PBF fuel rod	Isotopic Source Assay System	2.2 (accuracy)		L	665
PWR fuel rod	Subthreshold: moderated ^{252}Cf	1 to 1.5 (accuracy)		L	659
Rover fuel rods, 20 to 130 g ^{235}U per rod	Isotopic Source Assay System	3.5 (accuracy)		L	665
Rover fuel rods, 7 rods measured together	Subthreshold: isotopic photoneutron source	0.85	0.4	L	650

Note—See footnote at end of table.

Table 2.6 Uranium Assay of Feed and Product Materials (Cont'd)

Application	Method	Performance (% RSD)		Cross Reference	
		Random Error	Systematic Error	Source[a]	Handbook Page
SPERT fuel rod, 35 g ^{235}U per rod	Isotopic Source Assay System	2.3 (accuracy)		L	665
Spent fuel rods:					
LWR spent fuel assemblies	Delayed neutron: isotopic source step irradiation	5 (estimated)	5 (estimated)	L	641
	Subthreshold: moderated ^{252}Cf	5 (estimated accuracy)		L	659
MTR spent fuel element in a 5000-lb lead cask	Delayed neutron: 14 MeV neutrons	2 (accuracy)		L	632
$^{233}UO_2$-ThO_2 spent fuel rods	Reactor reactivity	0.5 (estimated accuracy)		L	711
Hot leached hulls	Gamma ray, NaI (^{144}Pr)	1 g U per ton of hulls (detection limit)		L	483
Uranium in waste contaminated with fission products in 55-gal. drums	Delayed neutron: isotopic source step irradiation	40 (estimated accuracy)		L	641

ATR = advanced test reactor; AVR = German pebble-bed reactor; BWR = boiling water reactor; DTPA = diethylenetriamine pentaacetic acid; EDTA = (ethylenedinitrilo) tetraacetic acid; FBR = fast breeder reactor; LWR = light water reactor; MTR = materials testing reactor; NBL = New Brunswick Laboratory; PBF = power burst facility; PWR = pressurized water reactor; SPERT = special power excursion reactor tests; TTA = thenoyltrifluoroacetone.

[a] E = Survey of exchange programs; L = literature survey; U = users' survey of production facilities.

[b] Includes sampling error.

Table 2.7 Uranium assay of solid scrap and waste materials

Application	Method	Performance (% RSD)		Cross Reference	
		Random Error	Systematic Error	Source[a]	Handbook Page
Clean Scrap, high concentration:					
U_3O_8 subblend, 75% U	Gravimetric	2.2[b]	0.023	U	194
Clinkers, 75% to 85%	Gravimetric	8.3[b] (1.3 to 19)	0.023	U	194
Hard scrap, 88% U	Gravimetric	0.014[b]	0.023	U	194
Laser fines, 88% U	Gravimetric	0.009[b]	0.023	U	194
Green pellets, 87% U	Gravimetric	0.30[b]	0.023	U	194
Green pellets, 84% U	Titrimetric: Davies and Gray/NBL	3.1[b]	0.035	U	201
Green scrap, 86% U	Titrimetric: Davies and Gray/NBL	1.0[b] (0.32 to 1.4)	0.035	U	201
U_3O_8 scrap blends	Titrimetric: Davies and Gray/NBL	0.85[b]	0.071	U	201
UO_2 scrap, 81.7% U	Titrimetric: Davies and Gray, visual	0.076	0.028	U	201
Miscellaneous scrap, high concentration:					
Recycle fines, U metal	Titrimetric: Davies and Gray/NBL	0.34[b]	0.018	U	201
Raw stock scrap, U metal	Titrimetric: Davies and Gray/NBL	2.3[b]	0.018	U	201
UAl_x, 70% U	Titrimetric: Davies and Gray/NBL	0.25 to 12[b]	0.018	U	201
U-Mo-Ru alloy, 0.2% to 80% U	X-ray fluorescence	0.27 to 84[b]	0.034	U	368
UO_2 powder/pellets/hard scrap, with $(NH_4)C_2O_4$ and NH_4HCO_3	Gravimetric	0.03 to 0.07	0.008	U	194
UO_2, U_3O_8	Gravimetric	0.02	—	U	194
UNH	Gravimetric	0.06	—	U	194
ADU/UO_2/U_3O_8, 67% to 80% U	Titrimetric: Davies and Gray/NBL	7.2[b] (2.4 to 10)	0.035	U	201

Note—See footnote at end of table.

Table 2.7 Uranium assay of solid scrap and waste materials (Cont'd)

		Performance (% RSD)		Cross Reference	
Application	Method	Random Error	Systematic Error	Source[a]	Handbook Page
UO_2 powder and scrap: UO_2 powder with GD_2O_3; UO_2 powder with $(NH_4)_2C_2O_4$ and NH_4HCO_3; wet/dry sludge; ADU; ash	Titrimetric: Davies and Gray, visual	4.4	0.037	U	201
UO_2 plus 2% to 5% Gd_2O_3 pellets and hard scrap	Titrimetric: Davies and Gray, visual	2.0	0.037	U	201
TRIGA waste: alloy, hydride, oxide	Titrimetric: Davies and Gray/NBL	2.6[b]	0.018	U	201
ADU, dry, 70% to 75% U	Titrimetric: Davies and Gray/NBL	3.5[b] (0.69 to 4.8)	0.035	U	201
ADU, wet, 50% U	Titrimetric: Davies and Gray/NBL	19[b]	0.035	U	201
LEU: dirty U_3O_8 scrap (>80% U) and ash (<60% U), 0.1 to 15 kg U per sample	Delayed neutron: 14 MeV neutrons	10	—	L	632
UO_2 hard scrap in 5-gal. cans, LEU	Isotopic Source Adjustable Fissometer	4.0 (accuracy)		L	666
Dirty scrap, high concentration:					
Floor sweepings, UO_2, 60% to 80% U	Titrimetric: Davies and Gray/NBL	13[b] (4.8 to 19)	0.035	U	201
Grinder sludge, UO_2, dry, 73% to 85% U	Titrimetric: Davies and Gray/NBL	5.3[b] (0.31 to 18)	0.035	U	201
Grinder sludge, UO_2, wet, 76% to 82% U	Titrimetric: Davies and Gray/NBL	5.0[b] (2.7 to 7.8)	0.035	U	201
Contaminated scrap, UO_2 57% to 78% U	Titrimetric: Davies and Gray/NBL	30[b] (3.5 to 39)	0.035	U	201

Note—See footnote at end of table.

Table 2.7 Uranium assay of solid scrap and waste materials (Cont'd)

Application	Method	Performance (% RSD)		Cross Reference	
		Random Error	Systematic Error	Source[a]	Handbook Page
Small press, 52% to 75% U	Titrimetric: Davies and Gray/NBL	23[b] (9.5 to 31)	0.035	U	201
Ash, 31% U	Titrimetric: Davies and Gray/NBL	19[b]	0.053	U	201
Calcined scrap	Titrimetric: Davies and Gray/NBL	9.1[b]	0.071	U	201
UO_2 dirty scrap, LEU in 5-gal. cans	Isotopic Source Adjustable Fissometer	5.0 (accuracy)		L	665
UO_2 press scrap, LEU in 5-gal. cans	Isotopic Source Adjustable Fissometer	3.5 (accuracy)		L	665
Saw sludge, 1-gal. can, bottle, up to 150 g	Gamma ray, NaI	4.4 to 13	4.2 to 8.9	U	418
Insolubles, ash, up to 200 g HEU, 24-in. diameter pan	Gamma ray, NaI	3.3	11	U	418
Dirty scrap/waste:					
Ash/calcine, LEU, scrap, up to 38 g, 5-gal. container	Gamma ray, NaI	6.6 to 14	2.7 to 17	U	418
Grinder ash and grit, HEU, up to 50 g ^{235}U, 5-gal. containers	Gamma ray, NaI	1.0 to 7.5	0.5 to 3.8	U	418
Residue, up to 143 g ^{235}U per sample	Isotopic Source Assay System	—	1.0 to 1.7	U	665
NaF residue, up to 142 g ^{235}U per sample	Isotopic Source Assay System	—	1.2	U	665
U/Th waste, 2-L and 5-gal containers, up to 60 g HEU	Segmented gamma ray, Ge(Li)	2.4 to 6.2	0.7 to 5.0	U	436
Combustible and noncombustibles, 3- by 7-in. cardboard cylinder, up to 38.0 g HEU	Gamma ray, NaI	1.1 to 3.5	9.4 to 17	U	418

Note—See footnote at end of table.

Table 2.7 Uranium assay of solid scrap and waste materials (Cont'd)

Application	Method	Performance (% RSD)		Cross Reference	
		Random Error	Systematic Error	Source[a]	Handbook Page
Combustible, plastic bag, up to 200 g HEU	Gamma ray, NaI	3.4	—	U	418
Combustible waste, noncombustible, cardboard box, up to 172 g LEU	Gamma ray, NaI	1.5 to 23	2.0 to 28	U	418
Noncombustible waste, residue, 2-qt poly bottle, up to 15 g LEU	Gamma ray, NaI	6.6 to 12	2.2 to 8.6	U	418
Combustibles in 55-gal. drums, 5 to 22 g ^{235}U per drum, LEU	Random Driver	6.7	7.9	U	605
Combustibles and noncombustibles, 55-gal. drums, up to 107 g HEU	Gamma ray, NaI	0.4 to 13	2.9 to 15	U	418
Combustibles and noncombustibles, 55-gal. drums, up to 30 g LEU	Gamma ray, NaI	1.8 to 20	3.4 to 10	U	418
Waste and scrap in 1 to 5-gal. cans 10 g to 1 kg U per can	Subthreshold: isotopic photoneutron source	2 to 10 (estimated)	1 to 3	L	650
Filter media, 9 to 50 g ^{235}U per sample	Isotopic Source Assay System	—	1.2	U	665
Pot hydride, product scrap, wet and dry fluid bed reactor scrap and cleanout, 1 gal. and smaller cans, 0.1 to 1.6 kg ^{235}U per can	Isotopic Source Assay System	6.0 (accuracy)		L	665
U_3O_8 process residue, HEU, 3-dram vial	Delayed neutron: Van de Graaff	1 to 2 3 (accuracy)	—	L	638
Sludge, HEU, 55-gal. drum, up to 15 g	Gamma ray, NaI	<16	3.5	U	418
Sludge, HEU, 2-L bottles, up to 60 g U per bottle	Isotopic Source Adjustable Fissometer	2.4	8.3	U	665
Diffusion plant residues, LEU, 0.16 to 31 kg U in a 7.6-L can	Neutron Well Coincidence Counter	5 to 15	—	L	507

Note—See footnote at end of table.

Table 2.7 Uranium assay of solid scrap and waste materials (Cont'd)

Application	Method	Performance (% RSD)		Cross Reference	
		Random Error	Systematic Error	Source*	Handbook Page
MOX waste, 5 gal. container, up to 15 g HEU	Gamma ray, Ge(Li)	1.8 to 11	2.7 to 3.6	U	418
Dirty scrap/waste, low concentration:					
HEU waste in large box (4 by 4 by 8 ft)	Gamma ray, NaI	19	—	U	418
LEU waste in large box (3.5 by 4 by 4 ft), up to 750 g U	Gamma ray, NaI (^{238}U daughters)	43 ("limit of error")		L	470
Waste in 55-gal. drum, up to 100 g HEU	Segmented gamma ray, Ge(Li)	2.2 to 5.1	0.5 to 4.4	U	436
Furnace parts and reduction residues, HEU in 30-gal. drums	Delayed neutron: isotopic source step irradiation	20 (accuracy)		L	641
Uranium residue, up to 0.6 g U	Gamma ray, NaI (well)	1.4 to 2.7	0.4 to 1.4	U	418
^{233}UO$_2$ in 55-gal. drum, up to 12.5 g	Gamma ray, NaI (^{232}U daughters)	6 to 7 (95% confidence limit)		L	470
HEPA filters, up to 33 g LEU	Gamma ray, NaI	1.2 to 10	0.47 to 7.5	U	418
HEPA filter, up to 11 g HEU	Gamma ray, NaI	—	1.3	U	418
HEPA filter, up to 20 g LEU	Random Driver	—	2.4	U	665
HEU filters in cardboard cartons, 15 g U per carton	Isotopic Source Adjustable Fissometer	3.9	9.6	U	665
Laundry, 55-gal. drum, up to 8 g LEU	Gamma ray, NaI	4.3 to 6.3	1.6 to 6.9	U	418

Note—See footnote at end of table.

Table 2.7 Uranium assay of solid scrap and waste materials (Cont'd)

Application	Method	Performance (% RSD)		Cross Reference	
		Random Error	Systematic Error	Source[a]	Handbook Page
Laundry, 55-gal. drum, up to 6 g HEU	Gamma ray, NaI	<24	1.7	U	418
Laundry, LEU, 55-gal. drum, up to 10 g	Random Driver	4.8	6.6	U	665

ADU = ammonium diuranate; HEPA = high-efficiency particulate air; UNH = uranyl nitrate hexahydrate.

[a] L = literature survey; U = users' survey of production facilities.

[b] Includes sampling error.

Table 2.8 Uranium assay of waste solutions

Application	Method	Performance (% RSD)		Cross Reference	
		Random Error	Systematic Error	Source[a]	Handbook Page
Miscellaneous uranium solutions:					
Uranium CO_3 streams	Spectrophotometric: 2,3-dihydroxy-naphthalene-6-sulfonic acid complex, continuous flow monitor, 8 to 60 μg/mL	9.9 to 1.1	—	L	244
Purex waste solution	Spectrophotometric: arsenazo III complex, 1 to 10 μg U	20 to 2	—	L	244
Low-level uranium solutions:					
Uranyl nitrate,	Titrimetric: Davies and Gray/NBL	13[b]	0.035	U	201
0.1 g U per g solution	Gravimetric	0.08	—	L	194
Uranyl nitrate waste, scrap	Titrimetric: Davies and Gray, visual	0.33	0.037	U	201
	Titrimetric: Davies and Gray/NBL	0.24[b]	0.071	U	201
Uranyl nitrate, HEU, 55-gal. drum, 2 to 100 g HEU	Gamma ray, NaI	0.6	0.7	U	418
Uranium solutions, HEU, 250-mL flask, 1 to 50 mg/mL	Gamma ray, NaI	10 (accuracy)		L	418
Uranium solutions, LEU, HEU, 50 mL vial, 0.2 to 6.0 mg/mL	Gamma ray, NaI	0.4	—	U	418
Uranium solutions, HEU 3-mL test tube, 0.006 to 5.0 mg/mL	Gamma ray, NaI (well)	1.0 to 20	0.82	U	418

Note—See footnote at end of table.

Table 2.8 Uranium assay of waste solutions (Cont'd)

Application	Method	Performance (% RSD) Random Error	Performance (% RSD) Systematic Error	Cross Reference Source[a]	Cross Reference Handbook Page
Uranium solutions, HEU, 100-mL vial, 0.005 to 2.0 mg/mL	Gamma ray, Ge(Li)	9.8	1.0	U	418
UNH, raffinate, UO_2F_2, miscellaneous aqueous/organic solutions	Titrimetric: Davies and Gray/NBL	0.63[b]	0.071	U	201
Aqueous solutions, 10 to 200 μg/mL	X-ray fluorescence	44 to 3.7	11 to 0.95	U	368
Waste solutions, NO_3, F	X-ray fluorescence	57[b]	—	U	368
Liquid discharge solutions, 0.2 to 50 μg/mL	Spectrophotometric: dibenzoylmethane complex	76[b]	0.51	U	244
Ammonium diuranate filtrate, 68 μg/mL	Spectrophotometric: peroxide complex	4.0[b]	—	U	244
Grinder water with suspended solids	Fluorometric: standard additions, 2000 μg U/g	23[b]	5.8	U	257
Miscellaneous solutions	Fluorometric: tetrapropylammonium extraction, 5 μg U/mL	13	—	L	257
	Fluorometric: tetrapropylammonium extraction, <0.2 μg U	7.2	—	U	257
	Fluorometric: ethyl acetate extraction, 0.1 to 0.5 mg U/g	6 to 5	—	L	257

Note—See footnote at end of table.

Table 2.8 Uranium assay of waste solutions (Cont'd)

		Performance (% RSD)		Cross Reference	
Application	Method	Random Error	Systematic Error	Source[a]	Handbook Page
Miscellaneous Solutions (Cont'd)	Fluorometric: ethyl acetate extraction, 0 05 to 50 μg U/g	11.3	—	L	257
	Fluorometric: TOPO extraction, 0.005 to 100 μg U/g	51 to 3.1	—	U	257
	Fluorometric: standard additions, 10 μg U/mL	14	3.6	U	257
	Fluorometric: direct, laser, 0.05 to 50 μg U/g	5.3	—	L	257

TOPO = tri-m-octylphosphine oxide.

[a] L = literature survey; U = users' survey of production facilities.

[b] Includes sampling error.

Table 2.9 Measurement of uranium holdup in process equipment

Application	Method	Performance (% RSD)		Cross Reference	
		Random Error	Systematic Error	Source[a]	Handbook Page
HEU holdup—diffusion plant:					
Pump	Gamma ray, NaI	15 and 46 g (detection limits)		L	570
Converter	Gamma ray, NaI	5 and 8 g (detection limits)		L	570
Seal	Neutron (SNAP)	65 g at 15 cm (detection limit)		L	597
LEU holdup—fabrication plant:					
Duct	Gamma ray, NaI	10 to 33 (total error)		L	590
Filter and dust	Gamma ray, NaI	16	23	U	590

SNAP = Shielded Neutron Assay Probe.

[a] L = literature survey; U = users' survey of production facilities.

Table 2.10 Uranium isotopic analysis

Application	Method	Performance (% RSD) Random Error	Performance (% RSD) Systematic Error	Cross Reference Source[a]	Cross Reference Handbook Page
Uranium metal, alloys:					
U metal, 93% ^{235}U	Mass spectrometry, surface ionization	0.017	—	U	264
U metal, HEU	Gamma ray, NaI	—	1.9	L	551
U alloy, 97% ^{235}U	Mass spectrometry, surface ionization	0.008	0.008	U	264
ATR/TRTR material, 93% ^{235}U	Mass spectrometry, surface ionization	0.008[b]	0.052	U	264
Uranium hexafluoride (UF_6):					
0.3% to 98% ^{235}U	Mass spectrometry, gas ionization, double standard method	0.14 to 0.005	—	U	279
3.1 to 97.7% ^{235}U, 5A cylinder	Gamma ray, NaI	—	3.3	L	551
1.3 to 3.1% ^{235}U, 2.5-ton cylinder, 30A/B cylinder	Gamma ray, NaI	—	5.3	L	551
	Neutron, SNAP	1.5	5.6, 6.5	L	585
0.7% ^{235}U	Mass spectrometry, gas ionization	0.027 (0.014 to 0.075)	—	E	279
	Mass spectrometry, gas ionization, single standard method	0.015	—	U	279
	Mass spectrometry, surface ionization	0.66 (0.036 to 1.8)	—	E	264

Note—See footnote at end of table.

Table 2.10 Uranium isotopic analysis (Cont'd)

Application	Method	Performance (% RSD)		Cross Reference	
		Random Error	Systematic Error	Source[a]	Handbook Page
1.7% ^{235}U	Mass spectrometry, gas ionization	0.044 (0.015 to 0.083)	—	E	279
	Mass spectrometry, surface ionization	0.38 (0.029 to 0.88)	—	E	264
UF_6 in piping, 2% to 3% ^{235}U	Neutron	—	1.3	L	585
3.1% ^{235}U	Mass spectrometry, gas ionization single standard method	0.012	—	U	279
Uranium tetrafluoride (UF_4), 93% ^{235}U	Mass spectrometry, surface ionization	0.032	—	U	264
Uranium oxide (U_3O_8):					
Subblend of various enrichments, 2.8% ^{235}U	Mass spectrometry, surface ionization	4.3[b]	0.059	U	264
Powder, 20% ^{235}U	Mass spectrometry, surface ionization	0.11	—	U	264
Powder, 93% ^{235}U	Mass spectrometry, surface ionization	0.019	—	U	264
Uranium dioxide (UO_2):					
Powder, 2.5% to 3% ^{235}U	Mass spectrometry, surface ionization	0.22 (0.046 to 0.68)	—	E	264
	Mass spectrometry, gas ionization	0.039	—	E	279

Note—See footnote at end of table.

Table 2.10 Uranium isotopic analysis (Cont'd)

Application	Method	Performance (% RSD)		Cross Reference	
		Random Error	Systematic Error	Source[a]	Handbook Page
Powder, 2.8% ^{235}U	Mass spectrometry, surface ionization	0.12, 0.28[b]	—	U	264
Powder, 0.2% to 4.4% ^{235}U, 18.9-L bucket	Gamma ray, NaI	0.6	—	L	551
Powder, pellets, scrap, 0.2% to 20% ^{235}U	Gamma ray, Ge(Li)	—	6 to 7	L	560
Powder, pellets, 1.8% to 4.0% ^{235}U	X-ray, gamma ray, high-purity germanium (hpGe)	—	<1	L	560
BWR fuel pellets	Multienergy californium assay system	1.5 (accuracy)		L	696
LEU and HEU oxides and ZrO_2 powder, pellets, and scrap, 1.4 to 3.6 g uranium oxide per sample	Delayed neutron: 14 MeV	1.6 (^{235}U) 1.3 (total U) (accuracy)		L	632
Pellets, 2.8% ^{235}U	Mass spectrometry, surface ionization	0.41[b]	0.059	U	264
Pellets, 1.1% and 4.0% ^{235}U	Neutron resonance	6.2 (total error)		L	713
Uranium carbide:					
HTGR/TRIGA feed, 70% ^{235}U	Mass spectrometry, surface ionization	0.07[b]	—	U	264
HTGR/TRIGA feed, 20% ^{235}U	Mass spectrometry, surface ionization	0.16[b]	—	U	264

Note—See footnote at end of table.

Table 2.10 Uranium isotopic analysis (Cont'd)

Application	Method	Performance (% RSD)		Cross Reference	
		Random Error	Systematic Error	Source[a]	Handbook Page
Uranium solutions:					
Standards:					
1.5% ^{235}U	**Mass spectrometry, surface ionization**	0.2, 0.4	—	L	264
1% to 50% ^{235}U	**Mass spectrometry, surface ionization**	0.15	0.063	U	264
1.5% to 4% ^{235}U	**Mass spectrometry, surface ionization**	0.14	0.061	U	264
3.0% ^{235}U	**Mass spectrometry, surface ionization**	0.067 (0.018 to 0.14)	0.054	U	264
49.4% ^{235}U	**Mass spectrometry, surface ionization**	0.009, 0.029	0.052	U	264
92% ^{235}U	**Mass spectrometry, surface ionization**	0.02	—	L	264
93.3% ^{235}U	**Mass spectrometry, surface ionization**	0.003, 0.007	0.005	U	264
97.7% ^{235}U	**Mass spectrometry, surface ionization**	0.013 (0.005 to 0.032)	0.004	U	264
LEU material:					
1.5% ^{235}U	**Mass spectrometry, gas ionization, single standard method**	0.039	—	L	279
1% to 5% ^{235}U	**Mass spectrometry, gas ionization, single standard method**	0.1	—	L	279
2% ^{235}U	**Mass spectrometry, gas ionization, double standard method**	0.014	—	L	279

Table 2.10 Uranium isotopic analysis (Cont'd)

Application	Method	Performance (% RSD)		Cross Reference	
		Random Error	Systematic Error	Source[a]	Handbook Page
2.01% ^{235}U	Mass spectrometry, gas ionization, absolute method	0.25	—	L	279
3.0% ^{235}U	Mass spectrometry, surface ionization	0.083[b]	0.062	U	264
Liquid sample, LEU	Gamma ray, NaI well	0.3 to 0.6	0.08 to 0.16	U	579
HEU material:					
89% ^{235}U	Mass spectrometry, surface ionization	0.001[b]	0.003	U	264
90.1% ^{235}U	Mass spectrometry, gas ionization, single standard method	0.17	—	L	279
92% ^{235}U	Mass spectrometry, gas ionization, double standard method	0.028	—	L	279
92.19% ^{235}U	Mass spectrometry, gas ionization, absolute method	0.011	—	L	279
93% ^{235}U	Mass spectrometry, gas ionization, single standard method	0.02	—	L	279
	Mass spectrometry, surface ionization	0.01	—	U	264
93.17% ^{235}U	Mass spectrometry, gas ionization, absolute method	0.03	—	L	279
97% ^{235}U	Mass spectrometry, surface ionization	0.015[b]	0.003	U	264

Note—See footnote at end of table.

Table 2.10 Uranium isotopic analysis (Cont'd)

Application	Method	Performance (% RSD)		Cross Reference	
		Random Error	Systematic Error	Source[a]	Handbook Page
Uranyl nitrate:					
2.8% ^{235}U	Mass spectrometry, surface ionization	0.40[b]	0.059	U	264
3% ^{235}U	Mass spectrometry, surface ionization	0.17 (0.048 to 0.44)	–	E	264
	Mass spectrometry, gas ionization	0.028	–	E	279
2 to 5% ^{235}U	Mass spectrometry, surface ionization	0.1	–	U	264
54% ^{235}U	Mass spectrometry, surface ionization	0.038	–	U	264
93% ^{235}U	Mass spectrometry, surface ionization	0.026	–	U	264
Uranium/plutonium oxide:					
Powder, 0.7% ^{235}U	Mass spectrometry, surface ionization	0.58 (0.51 to 0.66)	–	E	264
Pellets, 0.7% ^{235}U	Mass spectrometry, surface ionization	0.94	–	E	264
Uranium/plutonium carbides:					
Carbide, 72% ^{235}U	Mass spectrometry, surface ionization	0.014[b]	0.052	U	264
Carbide and oxide material, 38% ^{235}U	Mass spectrometry, surface ionization	0.31[b]	0.051	U	264

Note—See footnote at end of table.

Table 2.10 Uranium isotopic analysis (Cont'd)

Application	Method	Performance (% RSD)		Cross Reference	
		Random Error	Systematic Error	Source[a]	Handbook Page
Scrap:					
Scrap, 97% ^{235}U	**Mass spectrometry, surface ionization**	0.015[b]	0.003	U	264
Ash, 80% U_3O_8, 1% to 20% ^{235}U	**Gamma ray, Ge(Li)**	<1	—	L	551
Scrap, LEU	**Gamma ray, NaI well**	4.2	1.1	U	579
LEU, dirty U_3O_8 >80% U and ash, <30% U, 0.1-15 kg U per sample	**Delayed neutron: 14 MeV**	12(^{235}U)	—	L	632
Ash, 2.8% ^{235}U	**Mass spectrometry, surface ionization**	1.9[b]	0.059	U	264

[a] L = literature survey; U = users' survey of production facilities; E = survey of exchange programs.

[b] Includes sampling error.

Table 2.11 Plutonium assay of feed and product materials

Application	Method	Performance (% RSD)		Cross Reference	
		Random Error	Systematic Error	Source[a]	Handbook Page
Plutonium metal, alloys:					
Metal, alloys	Controlled-potential coulometry	0.17	0.045	U	314
		0.024, 0.025	—	E	314
	Titrimetric: Pu(VI)-Pu(IV) couple,	0.038	0.038	U	293
	amperometric end point	0.049	—	E	293
	Titrimetric: Pu(III)-Pu(IV) couple,	0.086	-	U	293
	spectrophotometric end point (ferroin)	0.021, 0.049	—	E	293
Metal button, 1.4 to 2.2 kg	Neutron counting (SNAP)	2	—	L	495
Metal button inventory samples in 1-gal. cans	Isotopic Source Assay System	4.2 (accuracy)		N	665
	Random Driver	2.6 (accuracy)		N	665
Plutonium fluoride:					
Inventory samples in 1-gal. cans	Isotopic Source Assay System	11 (accuracy)		N	665
	Random Driver	17 (accuracy)		N	665
Pu fluorides	Photofission: linear accelerator	7.6 (accuracy)		L	700
Plutonium green cake: Inventory samples in 1-gal. cans	Isotopic Source Assay System	0.9 (accuracy)		N	665
	Random Driver	6.8 (accuracy)		N	665

Table 2.11 Plutonium assay of feed and product materials (Cont'd)

Application	Method	Performance (% RSD) Random Error	Performance (% RSD) Systematic Error	Cross Reference Source[a]	Cross Reference Handbook Page
Plutonium dioxide (PuO_2):					
Powder	Controlled-potential coulometry	0.05	—	L	314
		0.019[b]	0.045	U	314
		0.26	—	E	314
	Titrimetric: Pu(VI)-Pu(IV) couple, amperometric end point	0.42[b]	0.038	U	293
		0.13[b]	0.11	U	293
		0.059	—	E	293
	Titrimetric: Pu(VI)-Pu(IV) couple, potentiometric end point	0.079, 0.098	—	E	295
	Titrimetric: Pu(III)-Pu(IV) couple, potentiometric end point	0.085 to 0.15	—	E	293
Powder, 900 g, can	Neutron well coincidence counter	4.5	—	L	507
Pellets	Titrimetric: Pu(VI)-Pu(IV) couple, amperometric end point	0.24[b]	0.11	U	293
Inventory samples in 1-gal cans	Isotopic Source Assay System	7.4 (accuracy)		N	665
	Random Driver	6.5 (accuracy)		N	665
Pu oxides	Photofission: linear accelerator	5.7 (accuracy)		L	700
Oxides, metal, MOX (20% Pu):					
In 404 tin can, 200 to 2200 g Pu	Calorimetry calibrated against chemistry	0.05 to 0.59 (Av: 0.17)	0.07 to 0.42 (Av: 0.22)	L	533

Note—See footnote at end of table.

Table 2.11 Plutonium assay of feed and product materials (Cont'd)

Application	Method	Performance (% RSD)		Cross Reference	
		Random Error	Systematic Error	Source[a]	Handbook Page
In 404 tin can, 200 to 2200 g Pu	Calorimetry and mass spectrometry	0.13 to 0.63 (Av: 0.3)	0.07 to 2.0 (Av: 0.5)	U/E	533
	Calorimetry, mass spectrometry, and alpha pulse height analysis	0.06 to 1.1 (Av: 0.4)	0.03 to 0.33 (Av: 0.15)	L	533
	Calorimetry, gamma-ray spectroscopy of solutions, and isotopic correlation	0.09 to 0.36	0.08	L	533
	Calorimetry, gamma-ray spectroscopy of solids, isotopic correlation	0.1 to 1.5	0.1 to 0.5	L/U	533
Plutonium solutions:					
Plutonium nitrate	Titrimetric: Pu(VI)-Pu(IV) couple, amperometric or potentiometric end point, 4 to 250 mg Pu	0.26 to 0.03	—	L	293
	Titrimetric: Pu(VI)-Pu(IV)couple, potentiometric end point	0.23, 0.24	—	E	293
	Titrimetric: Pu(III)-Pu(IV) couple, potentiometric end point	0.12 to 0.22	—	E	293
	Gravimetric	0.05 to 0.2	—	L	290
	Complexometric: EDTA	0.4 to 0.6	—	L	309
	Complexometric: diethylenetriamine pentaacetic acid	1.0 (accuracy)		L	309
	Controlled-potential coulometry	0.12, 0.21	—	E	314
	Spectrophotometric: Pu(III) at 565 nm	0.05	—	L	325
	Spectrophotometric: Pu(VI) at 830 nm, 7 to 140 mg/L Pu	2.0 to 2.9	—	L	325
	X-ray fluorescence	4.0	—	U	368

Table 2.11 Plutonium assay of feed and product materials (Cont'd)

		Performance (% RSD)		Cross Reference	
Application	Method	Random Error	Systematic Error	Source[a]	Handbook Page
Miscellaneous	Titrimetric: Pu(VI)-Pu(IV) couple, amperometric end point	0.36	0.11	U	293
		0.099, 0.24	—	E	293
	Titrimetric: Pu(III)-Pu(IV) couple, potentiometric end point, 25 to 600 mg Pu	0.1 to 0.02	—	L	293
	Titrimetric: Pu(III)-Pu(IV) couple, potentiometric end point, 4 to 50 mg Pu	2.25 to 0.2	—	L	293
	Titrimetric: Pu(III)-Pu(IV) couple, spectrophotometric end point (ferroin)	0.07 to 0.14	—	L	293
	X-ray fluorescence	1, 1.2	—	L	368
	Gross alpha: direct 2π gas proportional	1.8	—	U	336
	K edge absorptiometry, Ge(Li), 140 to 350 g/L	0.1	≤0.4	L	457
	Gamma ray, differential absorption, Ge(Li), 100 to 250 g/L, 10 L bottle	≤2	<5	L	436
Pu/Th carbide pellets	Titrimetric: Pu(VI)-Pu(IV) couple, amperometric end point	2.9[b]	0.038	U	293
Pu/U metal alloy: ingots, ≤4 kg each	Delayed neutron: isotopic source step irradiation	3 (accuracy)		L	641
Pu/U oxides:					
Powder	Controlled-potential coulometry	0.082, 0.088	—	E	314
	X-ray fluorescence	0.4		L	368
		8.5	—	U	368
	X-ray fluorescence: on-line assay	0.2, 0.5	—	L	368

Note—See footnote at end of table.

Table 2.11 Plutonium assay of feed and product materials (Cont'd)

Application	Method	Performance (% RSD)		Cross Reference	
		Random Error	Systematic Error	Source[a]	Handbook Page
	Titrimetric: Pu(VI)-Pu(IV) couple, amperometric end point	0.081	—	E	293
	Titrimetric: Pu(III)-Pu(IV) couple, potentiometric end point	0.17, 0.35	—	E	293
Pellets	Titrimetric: Pu(VI)-Pu(IV) couple,	0.62^b	0.038	U	293
	amperometric end point	0.14, 0.18	—	E	293
	Controlled-potential coulometry	0.15	—	L	314
		0.19	—	E	314
	Gamma-ray scan, Ge(Li)	0.3 to 0.4	—	L	551
FFTF pellets	Delayed neutron: 14 MeV neutrons, ^{238}U	0.6 (accuracy)		L	632
	Delayed neutron: 14 MeV neutrons, ^{239}Pu	1.4 (accuracy)		L	632
Pu/U carbides:					
Pellets	Titrimetric: Pu(VI)-Pu(IV) couple, amperometric end point	0.56^b	0.038	U	293
	Controlled-potential coulometry	0.29^b	0.045	U	314
$PuO_2 + UO_2 + C$	Controlled-potential coulometry	2.8^b	0.045	U	314
Pu/U solutions:	Controlled-potential coulometry	1.1	—	L	314
	Spectrophotometric: tetrapropylammonium complex, 2 to 20 mg Pu/mL	2.0 to 0.2	—	L	325
	Spectrophotometric: arsenazo III complex, 2 to 10 μg Pu	1.9 to 0.58	—	L	325
	Spectrophotometric: xylenol orange complex, 2 to 5 μg Pu/mL	0.3 to 0.1	—	L	325

Table 2.11 Plutonium assay of feed and product materials (Cont'd)

Application	od	Performance (% RSD)		Cross Reference	
		Random Error	Systematic Error	Source[a]	Handbook Page
	Spectrophotometric: Pu(VI) at 830 nm, 50 to 250 mg Pu/L	3 to 0.2	—	L	325
	Gross alpha: TTA extraction, organic phase analyzed	3 to 5	—	L	336
	Gross alpha: TTA extraction, aqueous back extraction analyzed	0.8	—	L	336
	Gross alpha: direct, 2π gas proportional	1.2	—	U	336
	Isotope dilution mass spectrometry, weight aliquots	0.35	—	L	360
	Isotope dilution mass spectrometry, volumetric aliquots	0.6	—	L	360
	Isotope dilution mass spectrometry resin bead method	0.9	—	L	360
Irradiated solutions	X-ray fluorescence	0.3 to 3	—	L	368
	X-ray fluorescence: automatic on-line	0.5 to 1	—	L	368
Fuel rods:					
$^{235}U/^{239}Pu$ fuel pins	Subthreshold, isotopic photoneutron source, ^{235}U	1[d]	—	L	650
	Subthreshold, isotope photoneutron source, ^{239}Pu	2[d]	—	L	650
$^{235}U/^{239}Pu$ fuel rods	Lead slowing down spectrometer, ^{235}U	5 (accuracy)		L	708
	Lead slowing down spectrometer, ^{239}Pu	5 (accuracy)		L	708

Note—See footnote at end of table.

Table 2.11 Plutonium assay of feed and product materials (Cont'd)

		Performance (% RSD)		Cross Reference	
Application	Method	Random Error	Systematic Error	Source[a]	Handbook Page
ZPPR fuel element, Pu-U-Mo alloy	Gamma-ray scan, Ge(Li)	0.25	0.04	L	418
Pu in MOX fuel rod (1 by 15 cm), 12 and 23 g Pu per rod	Neutron well coincidence counter	1.4	—	L	507
Spent fuel rods and solutions:					
Pu/U ratio in irradiated PWR assemblies	$^{134}Cs/^{137}Cs$ ratio	0.5 to 0.8	1.3, 2.0	L	483
	$^{154}Eu/^{137}Cs$ ratio	5.2, 6.8	5.6, 8.7	L	483
Pu/U ratio in dissolved fuel	$^{134}Cs/^{137}Cs$ ratio	0.5	1.2	L	483
	$^{154}Eu/^{137}Cs$ ratio	1.0	2.0	L	483

FFTF = fast flux test facility; MOX = mixed (uranium and plutonium) oxide fuel; ZPPR = zero power plutonium reactor.

[a] L = literature survey; N = unpublished data; U = users' survey of production facilities; E = survey of exchange programs.

[b] Includes sampling error.

[c] Interlaboratory bias.

[d] Estimated.

Table 2.12 Plutonium assay of scrap and waste materials

Application	Method	Performance (% RSD)		Cross Reference	
		Random Error	Systematic Error	Source[a]	Handbook Page
Dirty scrap, high concentration:					
Pu molten salt inventory samples, 1-gal. cans	Isotopic Source Assay System	7.9 (accuracy)		N	665
Pu slag, graphite scarfing, insulation glass, and ash heel, 1-gal. cans (Rocky Flats standards)	Isotopic Source Assay System	6.6	1.0	L	665
Pu solids, 0.001 to 100% Pu	X-ray fluorescence	0.63	—	L	368
PuO_2 powder, up to 150 g, in 1-qt can	Neutron well coincidence counter	4.4	3.0	U	507
PuO_2 powder, 0.43 g Pu/g	X-ray fluorescence	2.9	—	U	368
Pu in incinerator ash, 21 and 51 g standards, 0.5-L can	K edge absorptiometry	—	2	L	457
Pu in ash/graphite, 4-L container, 10 to 700 g Pu	Gamma ray, NaI, transmission correction	<16 (accuracy)		L	436
Pu in ash/fluorides/oxides, 1-gal. can, up to 500 g Pu per can	Segmented gamma-ray scan, Ge(Li)	2 to 4 (accuracy)		L	436
Pu process residues, 8 to 10 g per can	Neutron well coincidence counter	9	—	L	507
Pu ash, 5-gal. can	Photofission: linear accelerator	4.5 (accuracy)		L	700
Plutonium nitrate from ash leach, 0.5 to 5 g/L	Gamma-ray, Ge(Li)	0.5	1.3	L	436
Pu scrap:					
50 to 500 g, in 1-gal. containers	Calorimetry and mass spectrometry	0.28 to 1.0	0.1 to 0.65	L/U	533

Note—See footnote at end of table.

Table 2.12 Plutonium assay of scrap and waste materials (Cont'd)

Application	Method	Performance (% RSD)		Cross Reference	
		Random Error	Systematic Error	Source^a	Handbook Page
20 to 1200 g, in 1-gal. containers	Calorimetry, mass spectrometry, and alpha pulse-height analysis	0.25 to 1.3	0.08 to 0.39	U	533
	Calorimetry and gamma-ray spectroscopy of solutions	0.09 to 0.36	0.08	L	533
	Calorimetry and gamma-ray spectroscopy of solids	0.9 to 3.6	0.10 to 1.1	U	533
Dirty scrap/waste:					
Pu in several matrices, wet and dry, 25 to 195 g Pu per barrel	Photofission: linear accelerator	4.2 to 7.4	—	L	700
Pu scrap and waste standards, several wet and dry matrices, 55-gal. drums	Delayed neutron: 14 MeV neutrons	36 (accuracy)		L	632
Dirty scrap/waste, low concentration:					
PuO_2 in compacted waste, ≈29-L bag, up to 40 g Pu	Neutron well coincidence counting	7.6	3.6	U	507
PuO_2 in plastic waste, 2-L carton, up to 20 g Pu	Neutron well coincidence counting	11	13	U	507
Low level Pu (4 nCi/g) combustible, 5.6 to 7.0 kg waste in 60-L carton	*L* X-ray, NaI Multienergy Gamma Assay System	10 <50 (accuracy)	—	L	477
Pu combustibles, 55-gal. drums, 37 g Pu	Neutron counting, slab counter	37	—	L	495
Pu combustibles, 55-gal. drums, 0.16 g ^{240}Pu	Fast coincidence counting	16	—	L	520

Note—See footnote at end of table.

Table 2.12 Plutonium assay of scrap and waste materials (Cont'd)

Application	Method	Performance (% RSD)		Cross Reference	
		Random Error	Systematic Error	Source[a]	Handbook Page
Pu combustibles, 4-L can	Segmented gamma-ray scan, Ge(Li)	2.5 (accuracy)		L	436
Pu/MOX combustible, 5-gal. bucket, up to 15.0 g Pu	Gamma ray, Ge(Li)	3.7 to 12	4.5 to 5.8	U	418
HEPA filters up to 100 g Pu	Gamma ray, hpGe	1.6 to 22	1.6 to 6.0	U	418
Pu waste, homogeneous matrix, 1-gal. cans	Delayed neutron: 14 MeV neutrons	3 (accuracy)		L	632
Pu waste, heterogeneous matrix, 1-gal. cans	Delayed neutron: 14 MeV neutrons	8 (accuracy)		L	632
Pu-poor muds 10 to 1800 μg/g	X-ray fluorescence	10	—	L	368
Uranium solution, 400 g per liter, 0.4 g ^{239}Pu per liter	Gross alpha: direct 2π gas proportional	1.8	—	U	336

[a] L = literature survey; N = unpublished data; U = users' survey of production facilities.

Table 2.13 Measurement of plutonium hold-up in process equipment

		Performance (% RSD)		Cross Reference	
Application	Method	Random Error	Systematic Error	Source[a]	Handbook Page
Mixed oxide fabrication plant: Total holdup of 6 rooms	Neutron slab counter and gamma-ray, NaI		1.27, 1.5[b]	L	597
Other fabrication plants:					
2 glove boxes, 1 kg Pu per glove box	Neutron, SNAP		−16, −7[c]	L	597
3 glove boxes	Gamma-ray, NaI		14, −7, 9[c]	L	590

[a] L = literature survey.

[b] Neutron holdup/gamma-ray holdup.

[c] 100(NDA − recovered)/recovered.

Table 2.14 Plutonium isotopic analysis

		Performance (% RSD)		Cross Reference	
Application	Method	Random Error	Systematic Error	Source[a]	Handbook Page
Plutonium metal, alloys:					
0.01% ^{238}Pu	Mass spectrometry, surface ionization	20	—	U	342
93.8% ^{239}Pu		0.10	—		
5.8% ^{240}Pu		0.26	—		
0.3% ^{241}Pu		0.81	—		
0.03% ^{242}Pu		7.1	—		
Plutonium dioxide (PuO_2):					
Powder, 1.5% ^{241}Pu	Mass spectrometry, surface ionization	0.91 (0.52 to 1.4)	—	E	342
Powder, 86% ^{239}Pu	Mass spectrometry, surface ionization	0.024 (0.012 to 0.038)	—	E	342
Powder	Gamma-ray ratio, hpGe, 148 to 345 keV:			L	560
	^{239}Pu/^{241}Pu	1.1 to 3.7	—		
	^{241}Am/^{239}Pu	2.4 to 9.0	—		
Powder, 94% ^{239}Pu	Gamma-ray ratio, Ge(Li), 94 to 104 keV:			L	560
	^{238}Pu	0.7 to 5.1	2.5		
	^{239}Pu	0.013 to 0.17	0.03		
	^{240}Pu	0.2 to 2.3	0.33 to 0.62		
	^{241}Pu	0.1 to 1.2	0.88 to 1.3		
	^{241}Am	0.4 to 2.5	2.7 to 4		

Note—See footnote a: end of table.

Table 2.14 Plutonium isotopic analysis (Cont'd)

Application	Method	Performance (% RSD)		Cross Reference	
		Random Error	Systematic Error	Source[a]	Handbook Page
Plutonium solutions:					
0.001% to 100% isotope	Mass spectrometry, surface ionization	5 to 0.05	—	L	342
83% ^{239}Pu	Mass spectrometry, surface ionization	0.070 (0.013 to 0.14)	—	E	342
1.3% ^{241}Pu	Mass spectrometry, surface ionization	0.61 (0.30 to 1.0)	—	E	342
0.00012 to 0.25 atomic ratio, ^{x}Pu/^{239}Pu	Mass spectrometry surface ionization	3.8 to 0.054	—	E	342
0.01% ^{238}Pu	Alpha spectrometry, Si surface barrier detector/surface ionization mass spectrometry	2	—	L	353
93% ^{239}Pu	Gamma ray, hpGe, 43 to 200 keV:			U	579
	^{238}Pu	5	—		
	^{239}Pu	0.05	—		
	^{240}Pu	0.5	—		
	^{241}Pu	2	—		
Plutonium/uranium oxides:					
Powder, 88% ^{239}Pu	Mass spectrometry, surface ionization	0.031[b]	0.01	U	342
Powder, 1.7% ^{241}Pu	Mass spectrometry, surface ionization	0.83	—	E	342
Powder, 86% ^{239}Pu	Mass spectrometry, surface ionization	0.047	—	E	342
Powder, 71% to 87% ^{239}Pu	Gamma-ray enrichment meter, Ge(Li):			L	551
	^{238}Pu	1.0	—		
	^{239}Pu	0.3	—		

Note—See footnote at end of table.

Table 2.14 Plutonium isotopic analysis (Cont'd)

Application	Method	Performance (% RSD)		Cross Reference	
		Random Error	Systematic Error	Source[a]	Handbook Page
	^{240}Pu	4.3	—		
	^{241}Pu	0.3	--		
Pellets, 1.7% ^{241}Pu	Mass spectrometry, surface ionization	0.78	—	E	342
Pellets, 86% ^{239}Pu	Mass spectrometry, surface ionization	0.064	—	E	342
Reference materials	Gamma-ray ratios, 2 Ge detectors:			L	560
	$^{238}Pu/^{241}Pu$	1.6 to 7.6	2.4		
	$^{240}Pu/^{239}Pu$	2.1 to 3.7	2.0		
	$^{241}Pu/^{239}Pu$	1.2 to 2.7	1.3		
	$^{241}Am/^{239}Pu$	1.3 to 2.0	1.2		
Rods, pellets, Pu standard reference materials	Gamma-ray ratio, Ge(Li), 332 to 345 keV, $^{239}Pu/^{241}Pu$	1.3 to 1.6	—	L	560
Isotopic content of irradiated fuel: rods with burnup up to 10000 MWD/t	Neutron resonance:				
	^{239}Pu	4.3%[c]	—	L	713
	^{240}Pu	12%[c]	—		

[a] L = literature survey; U = users' survey of production facilities; E = survey of exchange programs.

[b] Includes sampling error.

[c] Bias versus chemistry.

CHAPTER 3

Bulk Measurement Methods

3.1 INTRODUCTION

This chapter describes measurement of total bulk amounts of matter (solid, liquid, and gas) without regard to special nuclear material (SNM) content or chemical composition. Bulk measurement systems include weight (or mass), volume, and flow measurements. These types of measurements are perhaps the most frequently used methods for process, production, and material control in the nuclear fuel processing industry. Bulk measurement offers several compelling advantages when compared to other types of measurement. Bulk measurements are nondestructive, relatively easily performed, rapid, quickly learned without specialized training, inexpensive, and applicable to a variety of materials. Their disadvantage, of course, is the nonspecificity of the measurement with regard to amount of SNM. Bulk measurements are used directly or with other measurements (such as chemical assay or radiometric nondestructive assay (NDA)) to provide material control and loss detection.

This chapter will focus on the applications and performance of weight, volume, and flow measurements for the control of SNM containing materials being processed in the nuclear industry.

3.2 WEIGHT AND MASS MEASUREMENT

3.2.1 Introduction

Weighing SNM-Bearing Materials

Weight measurement is the most accurate and precise of all bulk measurement methods and is widely used for measuring the bulk quantity of SNM-bearing materials including feed, in-process material, intermediate and final products, scrap, and inventory materials. Weight measurements are used for production, process, and quality control as well as for nuclear material control and accounting (MC&A). The measurements are nondestructive, rapid, and easily performed with minimal training.

The weighing operations usually include adjusting the scale to indicate zero weight when the scale platform is empty, measuring the weight of the empty vessel (tare weight), and measuring that same vessel containing SNM-bearing material (gross weight). The net weight of the SNM-bearing material is then the difference between the gross and tare weights.

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Some scales can be made to indicate zero weight with the empty vessel on the platform (taring the scale); thus measuring the filled vessel will yield the net weight directly.

Weight and Mass

Weight, unlike volume or other measures of bulk quantity, is unaffected by temperature or density changes and can be related to mass, a fundamental quantity of matter. Weight is the resultant force acting on a mass due to the gravitational attraction of Earth:

$$\text{weight (force)} = \text{mass} \times \text{acceleration of gravity}$$

The acceleration of gravity is constant at a specific location but is not constant all over the Earth. It decreases with altitude and with latitude. Local effects such as nearby iron or dense ore deposits can also affect the acceleration of gravity.

Because all weighing devices can be calibrated with readily available mass standards, traceable to the international measurement systems, the effects due to variation in the acceleration of gravity and other local factors can be essentially eliminated. Weight, therefore, can be related directly to mass.

Weighing Devices

The underlying principle of weight measurement is to balance exactly the downward force that results from Earth's gravitational attraction for an unknown mass with an equal and known force in the opposite (upward) direction. Scales and balances are devices used to perform weight measurements. There are many types of scales and several principles of operation for measuring the force exerted by gravity on the mass being weighed. In this chapter, weighing devices are classified as mechanical or electronic. Mechanical and electronic balances and scales are available commercially for a wide variety of applications and performance requirements. Mechanical scales were developed before electronic scales and have traditionally been widely used whenever high accuracy is required. Recently, however, electronic scales and balances have been greatly improved. They now exhibit precision and accuracy approaching that of mechanical sales. Although electronic scales are usually more expensive, they offer some advantages that are particularly useful for remote applications in the nuclear industry.

Control of Weighing Errors (Refs. 1 and 2)

Measurement control procedures are required to assess and control weighing errors. These procedures, detailed in ANSI N15.18-1975, are common to all weighing devices and weight measurements. Weighing devices should be inspected and calibrated with traceable mass standards at frequent intervals. Calibrated check weights similar in mass to the the production items being routinely measured should be used at least once a day to ensure calibration. The weighing operation for measuring check weights should be exactly that for weighing production items. If the measured value of the check weight falls outside control limits, the weighing device should be removed from service and recalibrated immediately. The reproducibility of the weighing device should also be monitored using replicate measurements of check weights and production items. The deterioration of reproducibility may be an indication that maintenance and/or cleaning is required. Regular inspection and routine maintenance should be performed to detect dust, corrosion, damage, and wear.

Mass standards, certified by the National Bureau of Standards, are readily available for calibrating weighing devices. These primary mass standards can be used directly for scale calibration or for calibrating traceable secondary or tertiary standards to be used, in turn, for calibration or as check weights.

Errors Common to All Weighing Methods (Refs. 3 through 6)

Some materials processed in fuel facilities exhibit a spontaneous loss or gain of weight that does not result in a loss of SNM. Weight changes can result from the following:

(1) Adsorption or desorption of water
(2) Oxidation or reduction reactions
(3) Chemical decomposition
(4) Loss of non-SNM volatile components
(5) Other reactions leading to a change in the SNM concentration of the material being weighed.

The use of weight measurements for material control of these unstable materials can lead to serious systematic errors. Due to the time dependence of the material weight, this weight cannot be compared to weight measurements taken at another time or combined with concentration measurements taken at another time to yield total SNM content.

Improper zeroing or taring of scales will lead to a systematic error equal to this displacement. The zero value (scale reading with nothing on the scale platform) should be checked and/or readjusted frequently. The tare weight (scale reading with empty vessel on the scale platform) should be carefully measured for each vessel used.

Scales that are not properly leveled or are located on unstable platforms can yield erroneous weight readings which can be both random and systematic in nature.

Scales, particularly mechanical scales, located in dusty or corrosive environments must be cleaned, checked for damage, serviced, and recalibrated frequently to avoid large errors. A control chart of balance reproducibility, both with the check weights and with items being weighed, should be maintained to provide early warning of the deterioration of the scale condition. Excessive vibration can damage the precision knife edges of scales, cause erroneous weight measurements, and make reading the scale difficult.

When two objects with the same mass but different volumes are weighed, the object with the larger volume will weigh less. The difference in weight is equal to the difference in volume multiplied by the density of the displaced air. This systematic error, often referred to as the "buoyancy effect," is usually small but can be significant when large differences in bulk density exist between the masses being weighed. Corrections should be made using the following equation:

$$W_{corr} = W_0 + (V_0 - V_{std})\varrho_{air} \tag{3-1}$$

where

W_{corr} = object weight corrected for buoyancy
W_0 = measured object weight
V_0 = displacement volume of the object
V_{std} = displacement volume of the standard weights
ϱ_{air} = density of air

The density of air varies with temperature, barometric pressure, and relative humidity, and must be determined locally at the time of the buoyancy corrections. As an example, the buoyancy correction for a type 48G cylinder of UF_6 (having a volume of 3.94 m^3 and a nominal weight of 13,880 kg) and the volume of the same "mass in brass" (1.65 m^3 for brass weights with a density of 8.4g/cm^3 at 20° C) is calculated as follows: For air with a density of 1.2 mg/cm^3,

$$\begin{aligned}\text{Buoyancy correction} &= (V_0 - V_{std})\,\varrho_{air}\\ &= (3.94 - 1.65)\,.0012 \times 10^6\ \text{g}\\ &= 2748\ \text{g}\end{aligned}$$

In general, buoyancy corrections should be estimated for each type of sample to be measured to evaluate the need for routine buoyancy corrections.

Errors due to rounding of data or readability of the weighing device can be a dominant source of random error for weight measurements. The total random variance for a weight measurement $\sigma^2_{w_t}$ is the sum of the inherent random variance of the weighing device σ^2_{inst} and the rounding variance $\Delta^2/12$, where Δ is the readability of the scale or rounding increment:

$$\sigma^2_{w_i} = \sigma^2_{inst} + \frac{\Delta^2}{12} \tag{3-2}$$

3.2.2 Mechanical Weight Measurement

Description of Method (Refs. 3 to 11)

There are three basic techniques used for mechanical weight measurements: direct comparison with standard weights, spring distortion, and load cells.

Direct Comparison With Standard Weights

The principle employed in direct comparison scales is based on the use of precise levers and includes beam and pendulum balances. When unknown weight is suspended from the end of a uniform beam supported by an accurately located fulcrum (e.g., a knife edge), the beam can be balanced with known weights suspended from the other end of the beam as shown in Figure 3.1. The beam is balanced, and the unknown weight W_1 is compared to known weights W_2, when

$$W_1L_1 = W_2L_2$$

$$W_1 = \left(\frac{L_2}{L_1}\right) W_2 \tag{3-3}$$

where L_1 and L_2 are the distances from the fulcrum to where the weights W_1 and W_2 are suspended from the beam, respectively.

However, in the example of Figure 3.1 even the smallest imbalance would cause the beam to move to a position 90° from the balanced position; therefore, a pendulum weight is usually used in addition to the beam, as shown for an equal arm balance in Figure 3.2. When the two equal arms of the beam are unbalanced, the beam will tilt and the pendulum weight

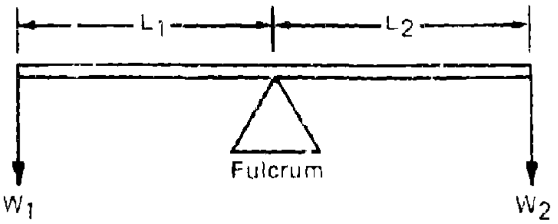


Figure 3.1 Balanced forces on a beam.

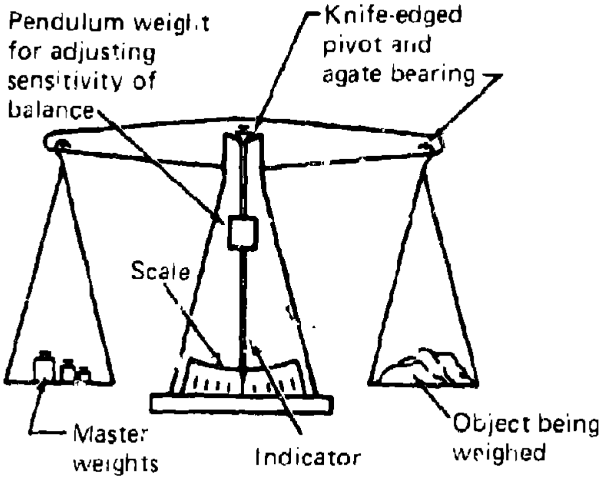


Figure 3.2 Equal arm balance.

will swing out a distance from the fulcrum and act as a counterweight (shown in Figure 3.3). As standard weights are added and the beam is

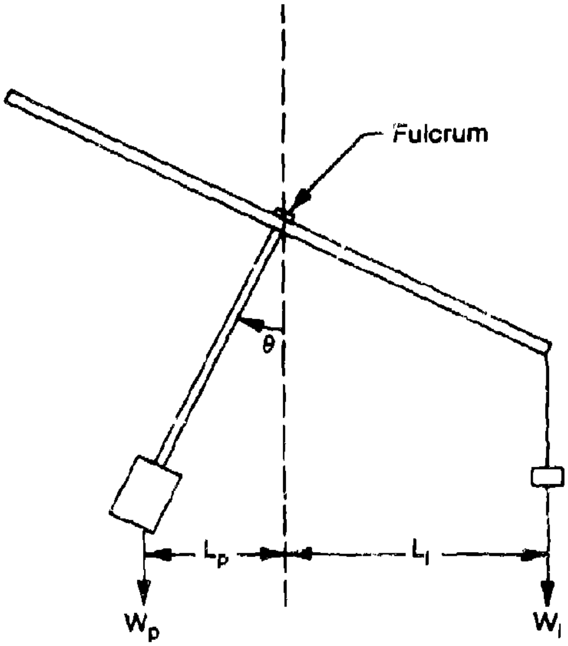


Figure 3.3 Principle of pendulum weight.

balanced, the pendulum will return to the neutral position under the fulcrum or knife edge. The length of the pendulum and its weight are used to adjust the sensitivity of the balance (the amount of beam deflection per unit weight imbalance).

The equal arm balance is the oldest known weighing device and, because of its sensitivity and simplicity of construction, it can be made the most accurate of weighing methods. Extremely accurate equal arm balances are used in the nuclear industry mainly to calibrate secondary and tertiary standard weights for routine measurement control programs.

Industrial beam-type scales, used routinely for measuring process items, are generally less accurate but more rapid and less susceptible to damage. This type usually has unequal arms with precisely located fulcrums that permit heavy objects to be weighed with small convenient counterweights.

In the beam scale shown in Figure 3.4, the force resulting from an unknown mass is measured by the position of a known weight, the counterpoise, on a graduated beam. The poise is moved by hand until the product of the unknown mass and the arm length is balanced by the fixed weight times the distance the poise was moved out onto the beam. The weighing range of these balances can usually be increased by adding known amounts of drop weights to the end of the beam.

$$W_1 = W_2\,(\text{fixed})\,\frac{L_2(\text{variable})}{L_1\,(\text{fixed})} + W_3\,(\text{variable})\,\frac{L_3\,(\text{fixed})}{L_1\,(\text{fixed})} \qquad (3\text{-}4)$$

Pendulum scales eliminate the need for such manual operations as adding standard weights to balance an equal arm balance or moving a poise to balance a beam-type scale. The pendulum scale shown in Figure 3.5 uses the same principles discussed earlier for levers.

When an unknown weight is placed on a pendulum scale, the force on one end of the lever supporting a pendulum weight automatically rotates the pendulum and moves the known pendulum weight (poise) away from the fulcrum until the unknown weight is balanced. The amount of pendulum movement can be measured by an indicator pointer driven by a rack and pinion. Some industrial scales use beam and pendulum concepts together. Most of the load is balanced with known weights added to the beam; the pendulum measures the additional weight required to balance the unknown weight.

Spring Scales

A spring is a body that deforms elastically in proportion to the amount of force applied to it (Hooke's Law). Coil springs, torsion bands, or beams of spring material can be designed to elongate, compress, bend, or flex a definite distance depending directly on the load applied.

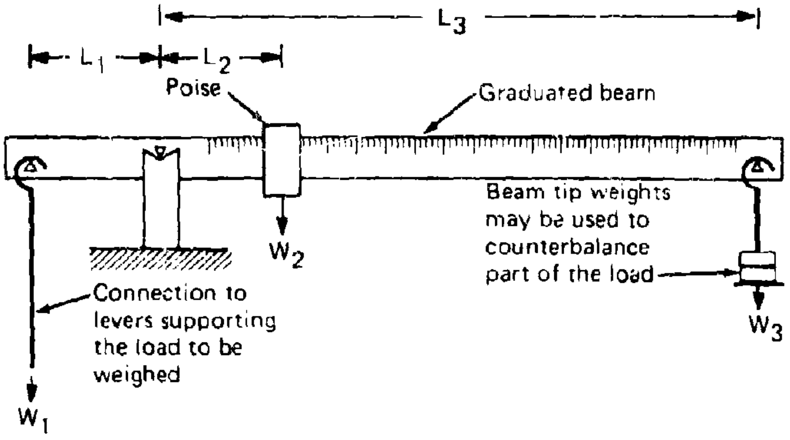


Figure 3.4 Beam scale.

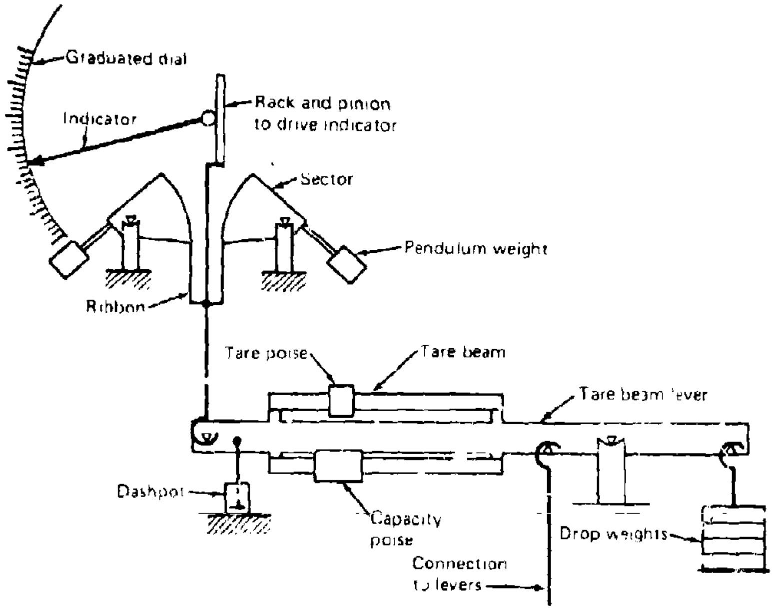


Figure 3.5 Pendulum scale.

Calibrating the deflection by relating to the amount of weight applied is the basic principle of the spring balance. The deflection can be measured mechanically, either directly or with rack and pinion magnification as shown in Figure 3.6a and Figure 3.6b. In both types, the object to be weighed is suspended or placed on a pan supported by a spring, and the deflection is related directly to weight using a previously calibrated dial.

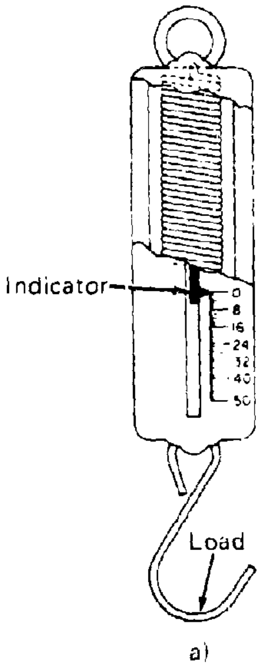
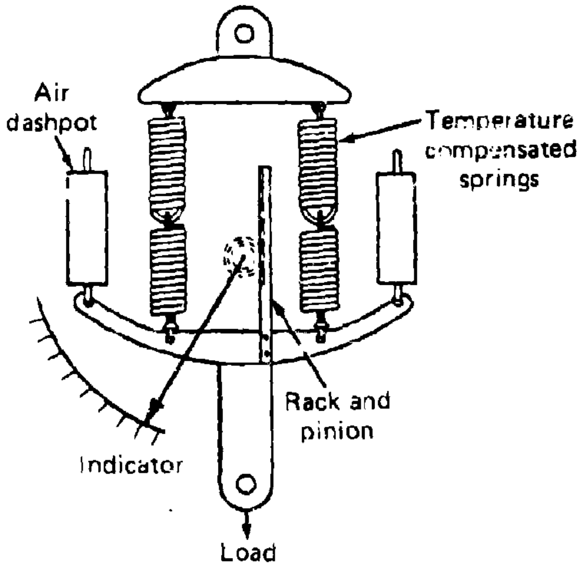


Figure 3.6a Spring scales – Deflection read directly.



b)

Figure 3.6(b) Spring scales—Deflection magnified by rack and pinion and read on a dial.

Mechanical Load Cells

When an object is placed on a hydraulic or pneumatic piston, shown in Figure 3.7, the increase in hydraulic or pneumatic pressure required to support the load is proportional to the weight of the object.

The pressure can be measured with a Bourdon tube or other pressure measuring devices that are calibrated to indicate weight. More than one load cell may be used in a weighing device, depending on the size of the objects to be weighed and the capacity of the scale. A totalizer sums the load on each of the load cells. (See Figure 3.8.) The hydraulic equipment thus performs a function similar to a mechanical lever, converting the load to an easily measured force.

Scope of Applications

Weight measurements can be effectively performed on any reasonably stable SNM-bearing materials including feed, intermediate and final products, inventory items, scrap, and waste materials.

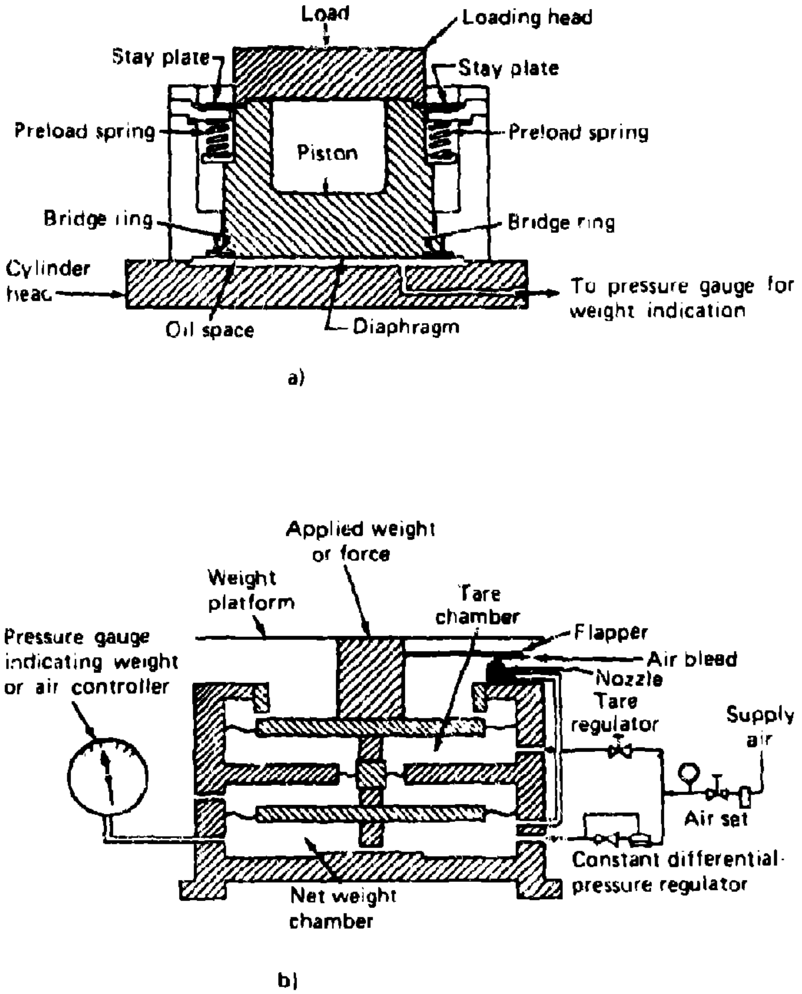


Figure 3.7 Mechanical load cells. (*a*) Hydraulic load cell. (*b*) Pneumatic load cell.

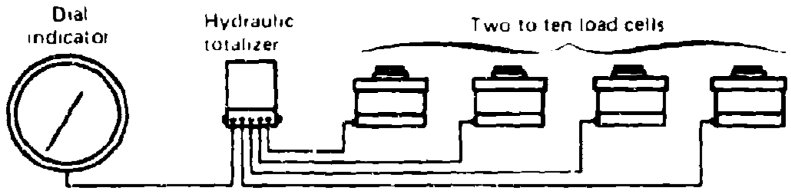


Figure 3.8 Hydraulic load cell totalizer.

Summary of Performance

See Table 3.1.

Equipment

Mechanical weighing devices with a wide range of operating principles, designs, performance, and costs are commercially available. The weighing devices should be selected to meet the requirements for specific applications. The size, shape, and weight of the items to be measured, the operation requirements, the environment under which the device is to be operated, and the required performance provide the primary basis for selection.

The weighing platform of the scale selected must be large enough to hold the item to be weighed, and the placement of the item on the platform should not significantly affect the random or systematic error of the weight measurement. It is usually recommended that the items to be weighed have weights in the upper indicating capacity of the weighing device. The readability and sensitivity of the device should be such that the random error is adequate to meet performance requirments. While readability is not a measure of the quality of the scale, the absolute random error of scales purchased from reputable manufacturers is usually near the quoted readability.

Accessories are available for most large mechanical scales. Printing attachments can record weight as well as time and other data on a ticket or strip to provide a record of the weighing. Analog to digital converters can be used to transmit weight information to remote printers or directly to computers for record or control purposes. However, care must be taken to ensure that these accessories do not degrade the performance of the scales.

Major Sources of Error

The major sources of error include:

(1) Unstable material (gains or loses weight)
(2) Improper zeroing of scale

(3) Unlevel scale or unstable scale support
(4) Excessive vibration
(5) Poor environment/improper maintenance
(6) Rounding error
(7) Buoyancy error
(8) Error in calibration weights and/or calibration procedure
(9) Poor weighing procedure

Because precision mechanical weighing devices are sensitive to their environments, care must be taken to provide environments relatively free from vibration, corrosive atmospheres, and dust. The support for the scale must be stable to permit careful leveling. Poor support or a poor environment can result in damage to the scales and poor performance. Scales should be inspected for damage and cleaned at regular intervals. Control charts on the daily check weights and on reproducibility of item weights can give early warning of the need for maintenance. (See also Section 3.2.1).

Measurement Control Requirements

The measurement control requirements for all weighing devices are described in ANSI N15.18-1975 (Ref. 1) and in section 3.2.1. Mechanical weighing devices should be calibrated with standard weights at least once per inventory period, and check weights should be measured frequently (depending on frequency of use) to ensure that the scale is still in calibration. Measurement of random error should be performed by making replicate weighings on production items. Control charts on the measured values of the check weights and the random error measurements should be maintained for each scale.

Data Analysis Requirements

Because scales read weight directly, calculations are simple:

$$\text{net weight} = \text{gross weight} - \text{tare weight}$$

All calculations can be performed with a simple calculator or by hand.

Survey of Selected Literature

There are very few reports in the literature on the applications and performance of mechanical weighing devices specifically related to SNM. Oak Ridge (Refs. 6 and 7) has studied the performance of several types of industrial scales for weighing UF_6 cylinders. Enriched uranium is processed as UF_6 and shipped to users in standard cylinders, which range widely in capacity as shown in Table 3.2. This study was performed because of the economic and strategic importance of controlling this

Table 3.1 Summary of Performance of Mechanical Scales

Capacity (kg)	Readability (g)	Evaluation Weight (kg)	Performance (% RSD)		Source
			Random Error	Systematic Error	
		Large mechanical scales			
18,000	2300	18,000	0.01	0.01	L
4500	450	2769	0.013	0.0047	U
		683	0.047	0.019	U
		635	0.030	—	U
		455	0.057	0.029	U
1145	100	700	0.016	0.0051	U
		580	0.019	0.0066	U
		30	0.10	0.10	U
		20	0.15	0.15	U
360	100	360	0.03	0.03	L
150	5	95	0.0065	0.0023	U
		50	0.012	0.0043	U
90	25	69	0.018	0.011	U
75	25	50	0.025	0.016	U
		22.5	0.056	0.035	U
60[a]	—	60	0.001	0.001	U
60[a]	—	60	0.0003	—	L
57	25	55	0.029	0.015	U
50	5	13	0.017	—	U
45	25	30	0.048	0.027	U
32	28	13.6	0.12	0.067	U
20	10	15	0.053	0.023	U

Note—See footnote at end of table.

Table 3.1 Summary of Performance of Mechanical Scales (Cont'd)

Capacity (kg)	Readability (g)	Evaluation Weight (kg)	Performance (% RSD)		Source
			Random Error	Systematic Error	
Mechanical top loading balances and scales					
13	1	10	0.0094	0.0029	U
		8	0.012	0.0036	U
		7	0.013	0.0041	U
		3.5	0.019	0.0082	U
		1.0	0.094	0.029	U
		0.5	0.19	0.058	U
10	1	10	0.013	0.0042	U
		5	0.013	0.0065	U
		2	0.043	0.018	U
		0.2	0.23	0.16	U
6	1	5	0.01	0.01	U
		1	0.05	0.031	U
5	0.1	3.0	0.0033	0.0012	U
		0.5	0.036	0.018	U
5	1.0	4.4	0.023	0.0085	U
		2.4	0.016	0.013	U
		1.3	0.017	0.022	U
3	0.1	2.5	0.0021	0.0012	U
		0.5	0.011	0.0024	U
1.2	0.01	1.2	0.00038	0.00026	U
		1.0	0.00045	0.00031	U
		0.8	0.00056	0.00039	U
		0.5	0.00090	0.00062	U

Note—See footnote at end of table.

Table 3.1 Summary of Performance of Mechanical Scales (Cont'd)

Capacity (kg)	Readability (g)	Evaluation Weight (kg)	Performance (% RSD)		Source
			Random Error	Systematic Error	
1.2 (cont'd)	001	0.3	0.0015	0.0010	U
		0.2	0.0022	0.0015	U
		0.1	0.0045	0.0030	U

L = Literature survey; RSD = relative standard deviation; U = users' survey of production facilities.

[a] Equal arm balance.

Table 3.1 Summary of Performance of Mechanical Scales (Cont'd)

Capacity (kg)	Readability (g)	Evaluation Weight (kg)	Performance (% RSD)		Source
			Random Error	Systematic Error	
1.2 (cont'd)	001	0.3	0.0015	0.0010	U
		0.2	0.0022	0.0015	U
		0.1	0.0045	0.0030	U

L = Literature survey; RSD = relative standard deviation; U = users' survey of production facilities.

[a]Equal arm balance.

Table 3.2 UF_6 cylinders

Cylinder Type	Gross Weight (lb)	Tare Weight (lb)	Net weight (lb) UF_6
48G	30,600	2600	28,000
48Y	32,760	5200	27,560
48X	25,530	4500	21,030
30B	6420	1400	5020
30A	6350	1400	4950
12A	645	185	460
12B	645	185	460
8A	375	120	255
5A	110	55	55
2S	9.1	4.2	4.9
1S	2.75	1.75	1

Sources: Refs. 6 and 7.

material, particularly for shipper/receiver agreement. These reports describe recommended calibration and scale control procedures for a variety of scales. Table 3.3 presents the performance of the scales for measuring both gross and tare weight of the UF_6 cylinders as well as the shipper/receiver agreement expected.

Scale manufacturers will supply a wealth of information about their weighing systems, including the expected precision and linearity of the results. Most manufacturers warrant their products to be accurate, with proper scale calibration, to the smallest dial graduation. The warranty establishes a tolerance interval on which weight acceptability is based within the mechanical limitations of the scale. The accuracy of the scale calibration is directly dependent on the accuracy of the standard weights and the calibration procedure.

Survey of Production Facilities

Every nuclear fuel fabrication plant surveyed made extensive use of mechanical weighing devices for material, process, and quality control weight measurements. Large capacity beam or beam and pendulum platform scales were used mostly to weigh UF_6 cylinders, uranium nitrate solution drums, and fuel assemblies in the weight range from 12 to 14,000 kg. Beam and pendulum bench scales and various types of mechanical top loaders were used mostly to weigh feed materials, intermediate products, and final fuel forms in the range from 0.5 to 30 kg. Large capacity equal arm two-pan precision balances (50 to 70 kg) were used for mass standardization. On occasion, the equal arm balances were used for highly accurate accountability purposes, but the time required to make the measurements was quite long for routine application.

Each of the users' survey random error values, presented in the section entitled "Summary of Performance," was calculated from 10 to 20

Table 3.3 UF_6 cylinder weighing performance

Weighing Device (Capacity)	Material Weighed	Evaluation Weight	Random Error	Shipper/Receiver Tolerance
Steelyard scale (40,000 lb)	UF_6 cylinders: 48A, 48F, 48G, 48X, 48Y	30,000 lb 5000 lb	2 lb 2 lb	20 lb 8 lb
Platform scale (10,000 lb)	UF_6 cylinders: 30A, 30B	5000 lb 1500 lb	2 lb 2 lb	8 lb 5 lb
Platform scale (800 lb)	UF_6 cylinders: 8A, 12A, 12B	125 to 600 lb	0.25 lb	—
Equal arm balance (60 kg)	UF_6 cylinders: 15, 25, 5A	1 to 50 kg	0.5 g	—
Fan scale (5 kg)	UF_6 cylinders: 15, 25	1 to 4 kg	0.5 g	—

Sources: Refs. 6 and 7.

sets of duplicate measurements of process materials taken on the same day or from 15 to 1300 replicate measurements of a mass standard taken over a period of 2 to 10 months. The random error of the scales, selected by the processors, seemed to depend mainly on their readability, regardless of capacity, as shown in Figure 3.9. The ratio of random error to readability averaged 0.72 for all scales with capacities from 1.2 to 4500 kg. This is not to suggest that the readability of a mechanical scale is a measure of its quality, but it does give an indication of the random error that can be expected from a high-quality scale relative to its readability under routine operational conditions. All scales surveyed were well maintained and under scale measurement control systems.

Each systematic error value, presented in Table 3.1, was calculated using replicate measurements taken on mass standards over a 2- to 10-month period. For comparison purposes, the systematic error, S_{sys}, was

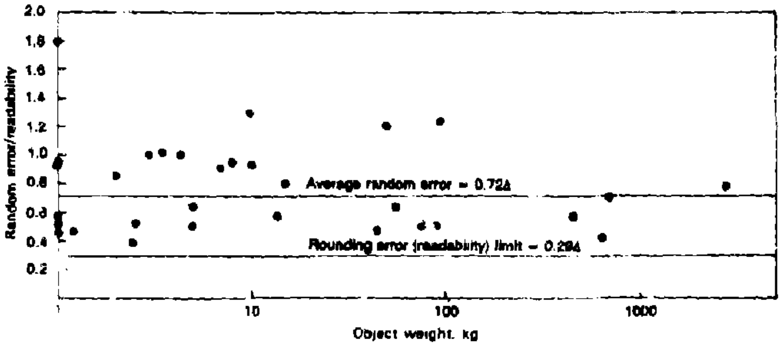


Figure 3.9 Random error of mechanical scales under routine production conditions (from survey of production facilities).

calculated from the reproducibility of these mass standard measurements but assuming only 15 measurements were made during the calibration run:

$$S_{sys}^2 = \frac{S_r^2}{15} + S_0^2 + \frac{\Delta^2}{12} \qquad (3\text{-}5)$$

where

S_r = standard deviation of the mass standard measurement
S_0 = uncertainty assigned to the mass standard
Δ = rounding interval (readability)

Figure 3.10 shows the ratio of systematic error to the readability (S_{sys}/Δ) for all the mechanical scales surveyed. These data indicate that the systematic error component of the measurements taken on these scales ($0.34\Delta \pm .04\Delta$) approaches the rounding error (0.29Δ) across the entire range of scale capacities (1.2 to 4500 kg).

Check weighings of mass standards are made routinely, at least twice each week and frequently more often, depending on the frequency of weighings on a particular instrument or the importance of the measurement. Initial calibration is performed with a set of mass standards that span the mass range of objects to be measured. Scheduled recalibrations are performed with frequencies ranging from once each week to once each 4 months. The standard masses are themselves remeasured against a master set of weights with a frequency equal to or less than once a year by an outside agency. All mass measurements are ultimately traceable to the National Bureau of Standards.

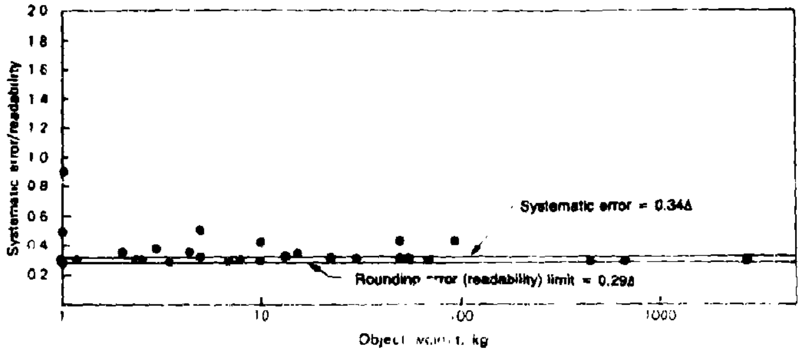


Figure 3.10 Systematic error of mechanical scales under routine production conditions (from survey of production facilities).

3.2.3 Electronic Weight Measurement (Refs. 12 to 18)

Description of Method

Four major techniques are used for electronic weighing: strain gauge, force compensation, vibrating wire system, and ferromagnetic load cells.

Strain Gauge Load Cells

The basic principle of the strain gauge load cell weight measurement is the electronic measurement of the deflection of a metal beam (spring) under load. Grids of wire or foils are bonded to the metal beam as shown in Figure 3.11. When the beam deflects under load, the electrical resistance of the grid or foil changes in direct proportion to the amount of deflection. The four strain gauges shown in Figure 3.11 are connected in the configuration of a Wheatstone bridge as shown in Figure 3.12. When a weight is placed on the beam, stain gauges A_1 and A_2 are shortened (resistance decreases) while B_1 and B_2 are lengthened (resistance increases). The Wheatstone bridge is then unbalanced and produces a dc voltage directly proportional to the weight applied.

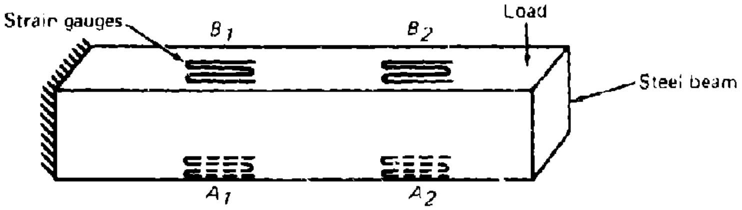


Figure 3.11 Strain gauge load cell, beam type.

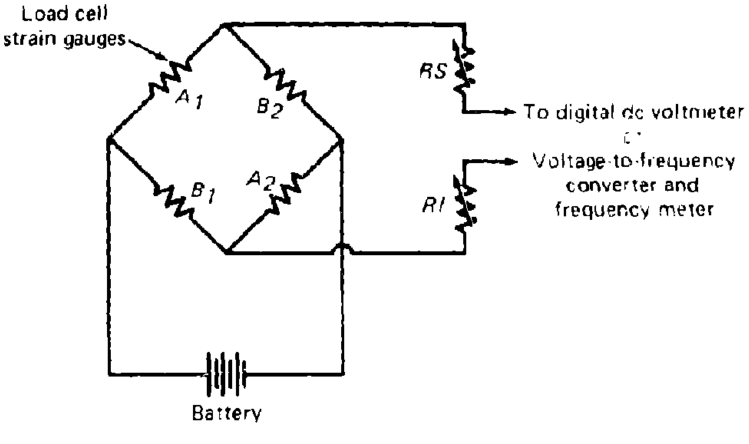


Figure 3.12 Wheatstone bridge, digital type.

Force Compensation

The basic principle of the force compensation system is that, when a current is passed through a load coil surrounding a magnetic pole piece, the two magnetic fields repulse each other and push the pole piece out of the coil. In a force compensation system, shown in Figure 3.13, the pole

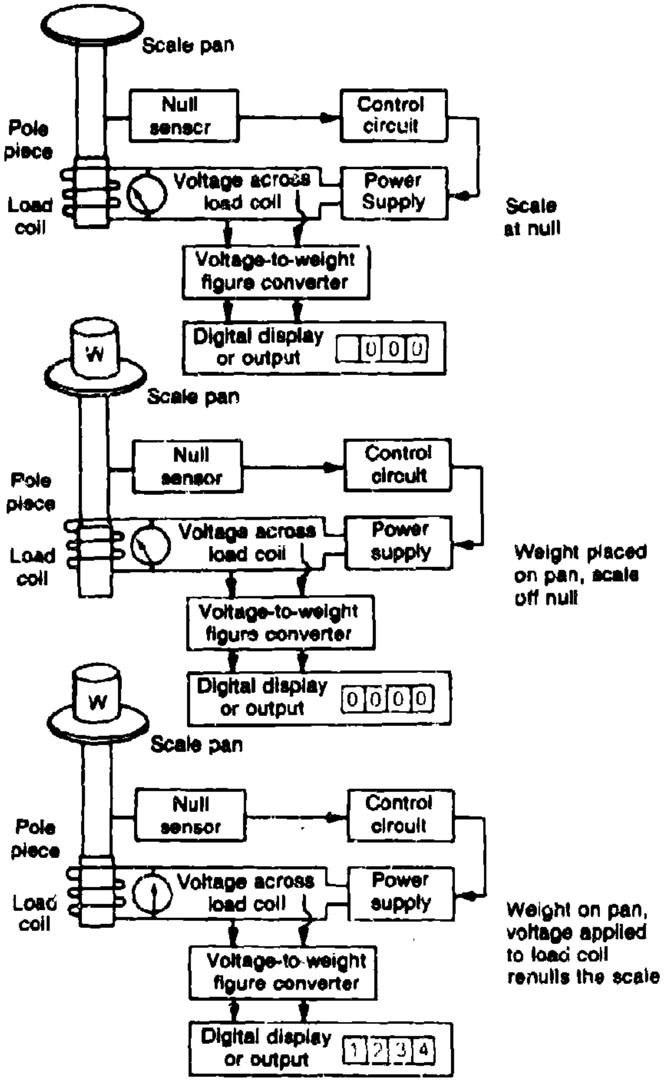


Figure 3.13 Force compensation system.

piece is connected to the weighing pan. The sysem senses the position of the pole piece, and when there is no weight on the pan, the sensor output registers null. When weight is added to the pan, the pole piece moves down to an off-null position. Through a control circuit, the sensor then increases the voltage to the coil, and the pan moves up until null is reestablished. The amount of voltage required to restore null is directly proportional to the weight placed on the pan. The actual movement of the pan is very small and the response time is very rapid.

Vibrating Wire Systems

The vibrating wire system is based on measurement of the resonant frequency of wires under tension. As more tension is applied to a wire, its resonant frequency increases. The system shown in Figure 3.14 compares the resonant frequency of a wire supporting a reference mass to the resonant frequency of a wire supporting the object to be weighed. The difference in the two frequencies is converted to output voltage and is directly proportional to the unknown weight.

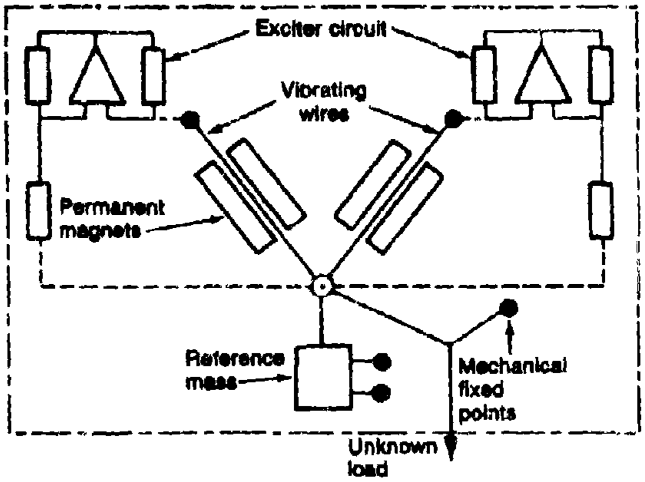


Figure 3.14 Vibrating wire system.

Ferromagnetic Load Cell

The ferromagnetic load cell is based on a special transformer to detect the deflection of a load-bearing member (spring material). When a weight is placed on the load-bearing member, it deflects and changes the relative position of the primary and secondary windings of the transformer. The voltage across the primary is not coupled to the secondary coil until a weight is added and the deflection occurs. The voltage output is directly proportional to the weight applied.

Scope of Applications

Electronic scales can be used to weigh any reasonably stable SNM material. Strain gauge load cells can be used to weigh very heavy materials, whereas force compensation scales are usually limited to weights under 30 kg because of power requirements. Force compensation scales are more sensitive to smaller weights than strain gauge load cells and tend to be more accurate.

Summary of Performance

See Table 3.4.

Required Equipment

Strain gauge load cell scales are readily available commercially with capacities from 1 kg to greater than 100 000 kg. Electronic top loaders using the force compensation load cell principles have become available recently with capacities from less than 100 g to about 30 kg.

Electronic scales have several advantages over mechanical scales. They can easily be adapted to perform remote measurements because their readouts can be separated from the load cells. Because the output is electrical (either analog or digital), these scales can be adapted to process control operations using the output as feedback. The load cell scales can be used to automatically collect and transmit the measurement data directly to a computer. (Binary coded decimal [BCD] output is available on newer models.) The more recent models also provide automatic zeroing and taring and are very rapid.

Electronic scales are less sensitive to vibration. Automatic integration is available to eliminate the effects of high-frequency vibration. When the electronics are separated from the load cell, the weighing operation can be performed in corrosive and dirty environments because the load cell can be sealed.

Selection of the type, capacity, and readability of the scale should be based specifically on the size and weight of the objects to be weighed and on the performance required. The weighing platform should be large enough to accommodate the items, and the scale performance should not be affected by the placement location on the platform. Accessories are available for remote readout, direct BCD output to computers, add-on microprocessors to process weight data automatically, remote or on-location printers, and data integrators for averaging data in high-vibration areas.

The cost of electronic scales depends on size and other factors, although they are more expensive than their mechanical counterparts.

Major Sources of Error

The major sources of error include (see also Section 3.2.1):

(1) Unstable material (gains or loses weight)
(2) Improper zeroing or taring error
(3) Hysteresis, particularly on strain guage load cells
(4) Improper maintenance
(5) Calibration error
(6) Buoyancy error
(7) Poor weighing procedure

Measurement Control Requirements

The measurement control requiremens are described in ANSI N15.18–1975 (Ref. 1). The scales should be calibrated at least once per inventory period, and a check weight should be measured at least daily on frequently used scales. The random error, calculated from replicate check weight and process sample measurements, should be monitored for each scale. Degradation of the random error may be an early indication of the need for maintenance and/or recalibration.

Data Analysis Requirements

Because readout is in weight, calculations such as gross minus tare and averaging are the only calculations involved. These can be performed easily by hand or with a small calculator. Built-in microprocessors are available for more complex programing and data reduction.

Survey of Selected Literature

Virtually no published data exist on the application and performance of electronic scales for measuring SNM. Most performance data must be gathered from manufacturers' literature. Table 3.5 summarizes a sampling of this type of information.

Table 3.4 Summary of Performance of Electronic Scales

Capacity (kg)	Readability (g)	Evaluation Weight (kg)	Performance (% RSD) Random Error	 Systematic Error	Source
		Large Strain Gauge Platform Scales			
4540	900	3182	0.054	0.016	U
		1818	0.066	0.022	U
		909	0.075	0.034	U
		682	0.092	0.044	U
		454	0.12	0.064	U
		228	0.19	0.12	U
100	5	62	0.026	0.0069	U
		26	0.028	0.0088	U
		10	0.045	0.018	U
50	5	41	0.014	0.0050	U
		30	0.013	0.0047	U
		21	0.015	0.0074	U
		15	0.013	0.0099	U
		10	0.021	0.015	U
		5	0.041	0.030	U
		5	0.29	0.29	U
		3	0.10	0.025	U
40	10	40	0.008	—	L
		20	0.016	—	L
		15	0.028	0.019	U

Note—See footnote at end of table.

Table 3.4 Summary of Performance of Electronic Scales (Cont'd)

Capacity (kg)	Readability (g)	Evaluation Weight (kg)	Performance (% RSD)		Source
			Random Error	Systematic Error	
		Electronic Top Loading Balances			
10	0.1	2.5	0.0011	—	U
10	1	10	0.015	0.0047	U
		7.3	0.014	0.0051	U
		5	0.037	0.011	U
		4	0.060	0.017	U
		2.3	0.025	0.014	U
		2	0.008	0.027	U
		0.2	0.41	0.18	U
		0.09	0.45	0.32	U
5	0.1	2.6	0.0029	—	U
5	0.5	5	0.0045	—	U
		4.5	0.0037	—	U
		2.5	0.0060	—	U
		2.1	0.0071	—	U
5	1.0	4.4	0.015	0.0073	U
		4.2	0.034	—	U
		2.7	0.053	—	U
		2.4	0.029	0.014	U
		0.7	0.081	0.045	U
1.2	0.01	0.2	0.006	0.005	U
		0.1	0.006	0.009	U
		0.07	0.007	0.007	U

L = literature survey; U = users' survey of production facilities.

Table 3.5 Literature survey performance of electronic scales

Type	Readability	Quoted Performance	
		Precision	Nonlinearity
Strain gauge platform scales	25 to 300,000 lb	0.02%	0.08%
	500 to 5000 lb	0.01%	0.08%
	10 to 25 lb	0.05%	0.16%
Force compensation electronic top loader	30 kg	0.5 g	1.0 g
	16 kg	0.05 g	0.1 g
	6 kg	0.05 g	0.1 g
	3 kg	0.05 to 0.005 g	0.01 to 0.1 g
	1.2 kg	0.05 to 0.005 g	0.01 to 0.001 g

Survey of Production Facilities

Electronic scales are currently being used in a number of nuclear fuel fabrication facilities. Strain gauge load cell scales are being used for large UF_6 cylinders and uranyl nitrate hexahydrate (UNH) drums as well as for smaller process objects in the 10- to 3200-kg weight range. The new electronic top loaders are being used for feed, process, and product measurements in the 1- to 30-kg weight range. The performance data for these applications are presented in Table 3.4. Each of the random error values was calculated from 10 to 20 sets of duplicate weight measurements on process items or 15 to 1300 replicate measurements on mass standards. As with the mechanical balances, the random error observed seems to be related to the scale readability for weight measurements in the 1 to 3200-kg range, as shown in Figure 3.15. The ratio of random error to scale readability for electronic scales varies greatly from 0.29 to 3.0 and averages about 0.99, compared to 0.72 for mechanical scales. All electronic scales surveyed were well calibrated, under scale measurement control programs, and in routine use.

The systematic variance S^2_{sys} was estimated from the standard deviation of the replicate standard measurements, assuming 15 calibration measurements were performed.

$$S^2_{sys} = \frac{S_r^2}{15} + S_0^2 + \frac{\Delta^2}{12} \qquad (3\text{-}6)$$

where

S_r = standard deviation of the mass standard measurements
S_0 = uncertainty assigned to the mass standard
Δ = rounding interval (readability)

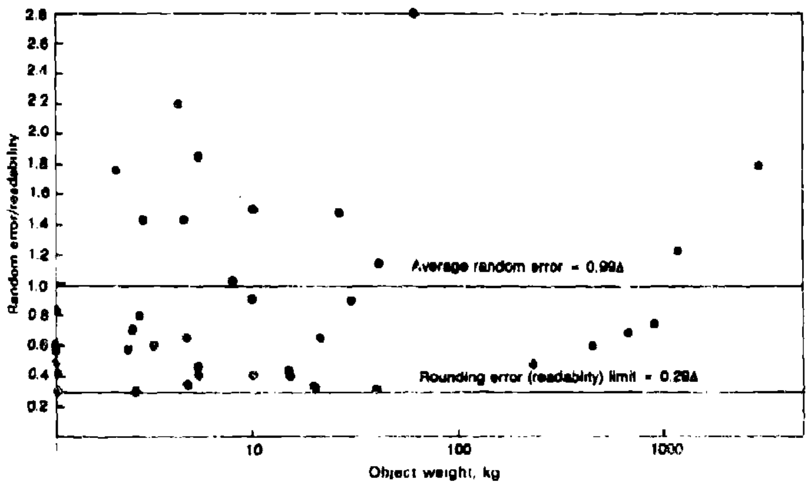


Figure 3.15 Random error of electronic scales under routine production conditions (from users' survey of production facilities).

Figure 3.16 shows the ratio of systematic error to scale readability for all measurements from 1 to 3200 kg. These data indicate that the systematic errors are almost totally dominated by the rounding error due to scale readability.

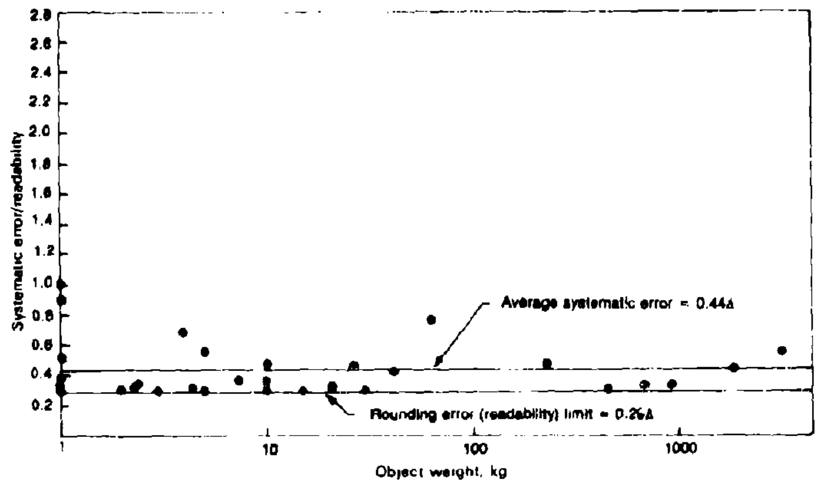


Figure 3.16 Systematic error of electronic scales under routine production conditions (from users' survey of production facilities).

3.3 VOLUME MEASUREMENTS

3.3.1 Liquid Level Methods

The most common method for determining the volume of liquid in a process tank is based on measuring the liquid level in the tank. If the tank configuration remains constant, the level of liquid in the tank can be related to volume by calibrating the tank with known volumes of liquid. Once the relationship between liquid level and volume has been established, the liquid level can be measured (by methods described in this section) and the volume calculated.

3.3.1.1 Calibration of Process Tanks

The calibration of process tanks for nuclear material control purposes should be based on standard volumes of liquid delivered by volumetric or gravimetric provers (measures) traceable to the National Bureau of Standards (NBS). NBS-certified volumetric provers are commercially available to deliver a wide range of volume increments. Gravimetric provers permit the liquid increment to be weighed. The calibration results obtained using these two methods of delivering standard volumes are equivalent, but the volumetric method is more convenient and is recommended by NBS (Ref. 19).

The calibration should be performed using established procedures suggested by the American National Standards Institute (Ref. 20) or by NBS (Ref. 21) to achieve traceable results. After the tank has been drained and cleaned, small increments of liquid are added to the tank from the prover. After each increment, the liquid level is measured. This procedure is repeated until the tank is filled. It is advisable to make several calibration runs to reduce the random error components of the calibration. The frequency of calibration depends on many site-specific factors. Based on the users' survey of production facilities, the tanks are usually recalibrated every 6 months to 2 yr.

At some facilities spot calibration checks are performed on tanks frequently. If these check calibration points fall outside acceptable limits, recalibration is performed immediately. Other facilities compare results among the various tanks during operations to determine whether recalibration is required. When liquid is transferred from one tank to another, the volume reduction in the first tank should be equal to the volume increase in the receiving tank. Recalibration is performed when these comparisons fall outside acceptable limits.

After the calibration data are corrected or normalized for temperature, density, or other factors described in the calibration procedures (Refs. 20 and 21), they are fitted to the calibration curve by the method of least squares. The form of the calibration equation depends on the physical configurations of the tank. When the tank is a right circular cylinder, the equation is linear:

$$H_2 = \alpha + \beta V \tag{3-7}$$

where

H_2 = liquid level in the tank
α = intercept constant
β = slope
V = volume of liquid in the tank (the sum of all volume increments added)

An example of a calibration curve is shown in Figure 3.17 (Ref. 22). The intercept is the "heel," which is the liquid that remains in the tank below the discharge tube. The cross-sectional area of some tanks, however, may vary with liquid level and, therefore, a series of linear equations or polynomial equations may be required. For example, a tank shown in Figure 3.18 has five separate regions. Region 1 is in the curved bottom of the tank below the differential pressure liquid level probe and

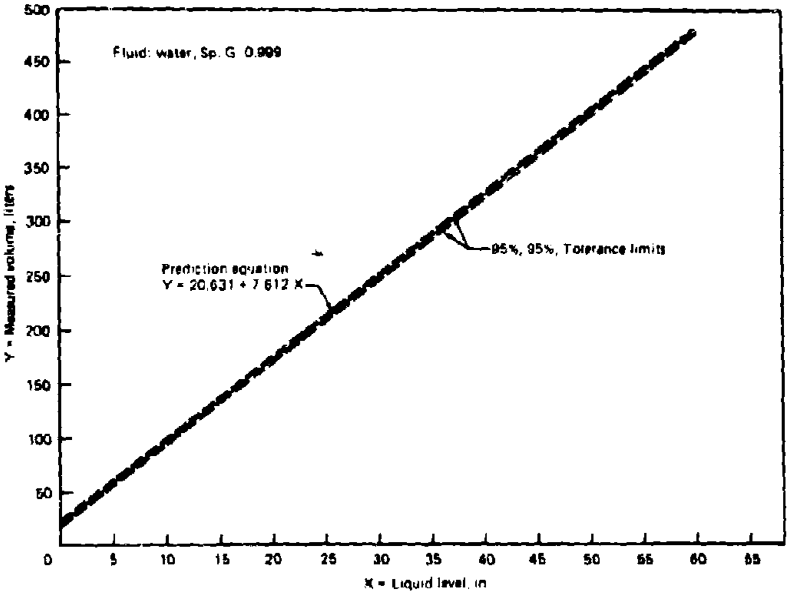


Figure 3.17 Linear calibration curve for process tank.

therefore would not be measured. This volume is the "measurement heel" of the tank and would have to be measured directly by draining the tank or by other methods (see Section 3.3.2). Region 2 is still in the curved portion of the tank and would require a nonlinear equation to fit the data. Regions 3 and 5 are straight-walled sections of the tank and could be described by a linear equation. Region 4 contains internal structure (cooling or heating coils) and would require a different equation. The data treatment should be designed to avoid calibration data in the immediate vicinity of the transition from one region to another. The calibration data in each region are then fitted to calibration equations separately.

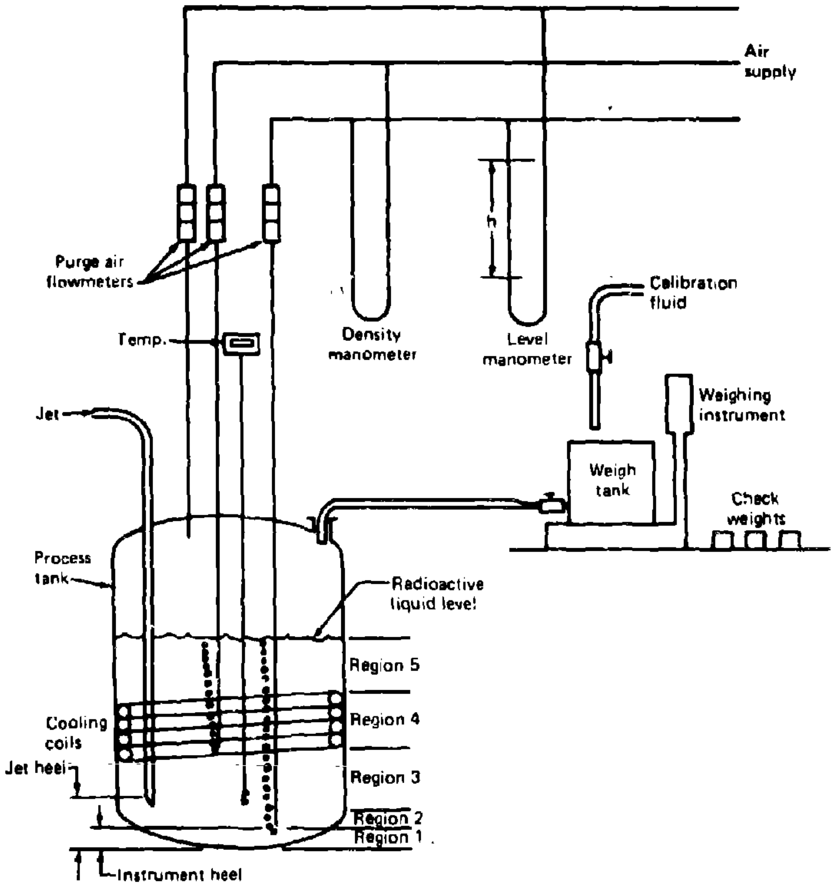


Figure 3.18 Schematic of instrumentation for tank calibration and volume determination.

Following the calibration and least-squares fitting of the data, the residuals of the curve fit should be carefully examined to ensure that the calibration equation adequately represents the calibration data. The residuals (observed minus calculated liquid levels) should be plotted against the volume added as shown in Figures 3.19 and 3.20. These residual data were collected during the users' survey of production facilities and demonstrate the need for examination of residuals. Figure 3.19 shows an instance when the least-squares fit to the calibration data is poor and can lead to systematic errors. The use of this calibration equation will lead to a bias at certain volumes in the process tank, and the systematic error tolerances will be unnecessarily large. Under these circumstances, another calibration equation (nonlinear or segmented linear) should be investigated prior to use of the tank or the calibration data. The residuals should be scattered randomly about zero all along the calibration curve as shown in Figure 3.20. The residual values can be used to determine the systematic errors that will result from the use of the calibration equation.

More detailed discussions of calibration and treatment of calibration data are found in Refs. 21 and 23 to 32.

3.3.1.2 Sight Gauges

Description of Method

The sight gauge is the most direct way of measuring the level of liquid in a process tank. This method is frequently used when the radioactivity level in and near the tank is low enough to permit access to the gauge.

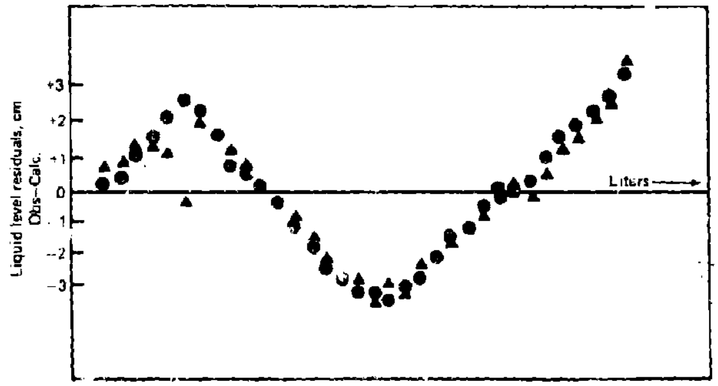


Figure 3.19 Plot of residuals from tank calibration showing poor fit of calibration data.

With the most common sight gauge, measurement is made by observing the liquid level in a graduated glass tube mounted on the exterior of the tank parallel to its vertical axis. At the bottom end, a connection is made between the glass tube and the tank contents. At the upper end a connection is made between the glass tube and the vapor space above the liquid.

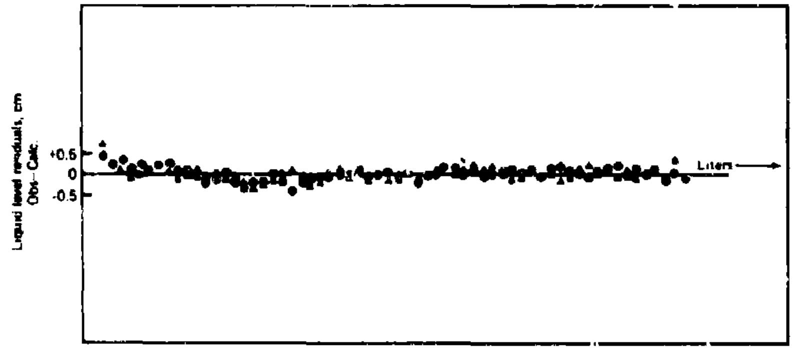


Figure 3 20 Plot of residuals from tank calibration showing an acceptable fit of calibration data.

Scope of Applications

Sight gauges are appropriate for measuring liquid levels when the amount of radioactivity is low enough to preclude radiation exposure hazard to personnel. The gauges must be located in an area readily accessible to the workers who must read them.

Where automatic data processing is required, or where a control room operation is necessary, use of sight gauges may not be feasible because they cannot easily be interfaced with a computer or remote readout devices.

Summary of Performance

Performance data for sight gauges are summarized in Table 3.6.

Equipment

The most common sight gauge is a calibrated glass tube mounted vertically on the exterior of the tank and connected both at the top and bottom. The liquid level in the tube is at the same level as it is in the tank. The glass tube is graduated, or a graduated steel rule is set in place behind the tube to measure the meniscus of the liquid. Various ruled increments are available, usually 0.1 to 1 cm.

Table 3.6 Summary of performance of sight gauges/graduated tanks[a]

Application	Sight Gauge Readability	Tank Volume (L)	Performance (% RSD)	
			Random Error	Systematic Error
Plutonium nitrate product tanks, Raschig ring filled	0.05 cm	9	—	2.1
	0.05 cm	30	—	0.67
	0.05 cm	31	—	0.32
	0.05 cm	185	—	0.65
	0.05 cm	200	—	0.45
	0.05 cm	210	—	0.76
	0.05 cm	222	—	0.67
	0.05 cm	225	—	0.13, 0.93
	0.05 cm	230	—	0.22
	0.05 cm	235	—	0.26
	0.05 cm	238	—	0.25
	0.05 cm	240	—	0.75
	0.05 cm	255	—	0.16
	0.05 cm	265	—	0.38
	0.05 cm	270	—	0.44
	0.05 cm	280	—	0.89
	0.05 cm	360	—	0.36
	0.05 cm	390	—	1.6
	0.05 cm	400	—	0.33, 0.83
	0.05 cm	405	—	0.40, 0.54
	0.05 cm	410	—	0.29, 0.39
	0.05 cm	420	—	0.29, 0.31
	0.05 cm	440	—	0.59
	0.05 cm	460	—	0.22
	0.05 cm	478	—	0.19

Note—See footnote at end of table.

Table 3.6 Summary of performance of sight gauges/graduated tanks[a] (Cont'd)

Application	Sight Gauge Readability	Tank Volume (L)	Performance (% RSD)	
			Random Error	Systematic Error
Plutonium nitrate product tank, Raschig ring filled (Cont'd)	0.05 cm	480	—	0.13
	0.05 cm	482	—	0.10, 0.27
	0.05 cm	483	—	0.39
	0.05 cm	505	—	0.44
	0.05 cm	510	—	0.14
	0.05 cm	560	—	0.29
	0.05 cm	565	—	0.28
	0.05 cm	570	—	0.28
	0.05 cm	610	—	0.08, 0.16
	0.05 cm	900	—	0.21
Plutonium nitrate waste/scrap tanks and side stream traps, Raschig ring filled	0.05 cm	22	—	0.91
	0.05 cm	26	—	1.2
	0.05 cm	31	—	0.64
	0.05 cm	100	—	0.80
	0.05 cm	175	—	0.63
	0.05 cm	180	—	0.22
	0.05 cm	190	—	0.42
	0.05 cm	195	—	0.21, 0.46
	0.05 cm	210	—	1.29
	0.05 cm	215	—	0.70, 0.60
	0.05 cm	218	—	0.51
	0.05 cm	225	—	0.31
	0.05 cm	230	—	0.22, 0.22
	0.05 cm	260	—	0.19

Note—See footnote at end of table.

Table 3.6 Summary of performance of sight gauges/graduated tanks[a] (Cont'd)

Application	Sight Gauge Readability	Tank Volume (L)	Performance (% RSD)	
			Random Error	Systematic Error
Plutonium nitrate waste/scrap tanks and side stream traps, Raschig ring filled (Cont'd)	0.05 cm	265	—	0.26
	0.05 cm	290	—	0.17
	0.05 cm	310	—	0.32, 0.39
	0.05 cm	340	—	0.38
	0.05 cm	370	—	0.054
	0.05 cm	375	—	0.67
	0.05 cm	380	—	0.13
	0.05 cm	390	—	1.05
	0.05 cm	430	—	0.40
	0.05 cm	505	—	0.44
	0.05 cm	520	—	0.46
	0.05 cm	550	—	0.21
	0.05 cm	565	—	0.28
	0.05 cm	800	—	0.15
	0.05 cm	840	—	0.33
	0.05 cm	875	—	0.31
	0.05 cm	1550	—	0.29
	0.05 cm	1560	—	0.40
	0.05 cm	2320	—	0.22
High enriched uranium solution, 5-in.-diameter glass columns, no Raschig rings	0.1 cm	12[b]	0.038	—
	0.1 cm	22[c]	0.029	0.094
	0.1 cm	22[d]	—	0.78

Note—See footnote at end of table.

Table 3.6 Summary of performance of sight gauges/graduated tanks[a] (Cont'd)

Application	Sight Gauge Readability	Tank Volume (L)	Performance (% RSD) Random Error	Performance (% RSD) Systematic Error
High enriched uranium solutions, Raschig ring filled	0.1 cm	75	0.25	1.44
	0.1 cm	76	0.30	0.34
	0.1 cm	78	0.13	0.38
	0.1 cm	79	0.14	0.16
	0.1 cm	81	—	0.45
	0.1 cm	84	0.14	0.34
	0.1 cm	84	—	0.45
	0.1 cm	85	0.13	0.38
	0.1 cm	139	0.10	0.19
	0.1 cm	152	0.09	0.11
	0.1 cm	153	0.09	0.12
Low enriched uranium solutions, scrap recovery tanks, Raschig ring filled	0.12 in.	315	0.83	—
	0.25 in.	315	0.88	0.34
	0.25 in.	337	2.79	1.02
	0.25 in.	364	1.13	0.86
	0.25 in.	403	3.42	1.21
	0.25 in.	412	3.45	1.34
	0.25 in.	423	2.86	0.60
	0.25 in.	461	1.56	0.57
	0.25 in.	479	1.29	0.55
	0.25 in.	486	1.07	0.44
	0.25 in.	494	1.50	0.59
	0.25 in.	506	1.42	0.57
	0.25 in.	554	0.71	0.26

Note—See footnote at end of table.

Table 3.6 Summary of performance of sight gauges/graduated tanks[a] (Cont'd)

Application	Sight Gauge Readability	Tank Volume (L)	Performance (% RSD)	
			Random Error	Systematic Error
Low enriched uranium solutions, scrap recovery tanks, Raschig ring filled (Cont'd)	0.25 in.	558	1.33	0.55
	0.25 in.	563	1.97	0.63
	0.25 in.	574	2.20	0.74
	0.25 in.	579	0.85	0.43
	0.25 in.	627	0.71	0.26
Water calibration tank	0.25 in.	97	—	0.087
Sight gauge performance test:[f]				
3-m	0.1 cm	Full scale	0.014	—
1.4-m	0.1 cm	Full scale	0.1	0.05
0.767-m	0.1 cm	Full scale	0.54	0.18

[a] Source of data for this table is users' survey of production facilities except where noted by footnote f.

[b] 1 tank.

[c] 2 tanks.

[d] 6 tanks.

[e] 14 tanks.

[f] Source of data is literature survey.

Other types of site gauges that can be used to measure liquid level are graduated glass or plastic tanks; a graduated, transparent strip mounted in the wall of the tank, or a transparent porthole with a fill-to-mark graduation. The liquid level in the tank can be observed directly with these methods.

The sight gauge must be mounted in an appropriate position to be accessible for direct reading. Adequate shielding should be installed to protect operators from radiation while the liquid level readings are performed.

Two important factors in achieving reliable sight glass readings are (1) accurately reading the level of liquid in the sight glass, and (2) observing the temperature and density differences between the liquid in the sight glass and the liquid in the process tank (Ref. 29).

Devices are available to assist in reading the sight glass more accurately by eliminating errors caused by parallax in measuring the meniscus of the liquid in the sight gauge. These devices range in sophistication from squares that slide up and down on the sight glass to telescopes that use a horizontal crosshair to track the bottom of the meniscus.

To ensure that the liquid in the sight glass is not at a temperature or density different from the liquid in the process tank, the system must be designed to permit the sight gauge contents to be removed and replaced with fresh liquid from the process tank. This is done by pressurizing the sight gauge to a pressure higher than the tank head pressure, thereby forcing the liquid back into the tank. When the pressure is removed, fresh liquid at the same temperature and density as that in the tank returns to the sight gauge (Ref. 29).

Major Sources of Error

The sight gauge can be considered a manometer with the sight glass representing one leg and the process tank the other. The liquid in the sight gauge is exposed to ambient temperature. If the ambient temperature is different from the temperature in the process tank, a difference in density between the liquid in the two legs can occur, resulting in an error.

The relationship between the density and height of the liquid in the sight glass and in the process tank is

$$H_1 = \frac{\varrho_2 H_2}{\varrho_1} \tag{3-8}$$

where

H_1 = height of liquid in the process tank
H_2 = meniscus height in the sight glass
ϱ_1 = liquid density in the process tank
ϱ_2 = liquid density in the sight glass

Anything that affects the density ratio ϱ_2/ϱ_1, such as temperature or concentration differences, will affect the reliability of the measurement. A difference of 10°C in the two liquids could create an error in the uncorrected value of 0.3%, assuming the density of water. Pressure cycling the liquid in the sight glass, as discussed previously, can eliminate the temperature difference.

The impact of error in a sight gauge measurement is reduced as the length-to-volume ratio of the tank is increased. This relationship between error and tank geometry applies to all liquid level measurements.

Measurement Control Requirements

The tanks should be drained, cleaned, inspected, and recalibrated at least once a year. Several calibration runs should be performed while the tank is out of service. Calibration procedures are described in Refs. 20 and 21 and are summarized in Section 3.3.1.1.

The tanks should be flushed and cleaned from time to time during routine operations to avoid sludge accumulation. Each time a volume increment is transferred to another tank, the decrease in the volume of the first tank should be compared with the volume increase in the second tank. These values should be charted and monitored. If values remain in control, it may not be necessary to recalibrate as frequently as has been suggested.

Data Analysis Requirements

Temperatue correction, the least-squares fitting of calibration data, and conversion of liquid level to volume is more conveniently performed by a computer but these calculations can be performed with a small calculator.

Survey of Selected Literature

The results in Table 3.7 show a wide range of random and systematic errors that cannot be completely explained. For example, at NBS (Ref. 29), a 0.014% random error (which includes the tank configuration error) was achieved with a sight glass, compared with 0.54% at the Rocky Flats Plant (Ref. 33). A partial explanation for this difference is that the percent random error for the data at NBS (Ref. 29) is for a full-scale value almost four times the size of the graduated scale used at Rocky Flats (Ref. 33). The variation in the absolute random error between the NBS and RFP data is approximately a factor of 10. The standard deviation corresponding to measurement errors, for which the tank configuration (i.e., the departure from right circular geometry) was canceled out, was calculated for the NBS data and is recorded in parentheses below the standard deviation of the residuals. The tests at NBS (Ref. 29) were conducted with a tank 4 ft (1.22 m) in diameter and 14 ft (4.27 m) high to compare three different pressure gauges and a sight glass. A sight glass having a 25-mm bore in direct contact with a measuring tape was mounted vertically on the exterior wall of a 300-L tank containing water.

In the study performed at Westinghouse (Ref. 22), uranyl nitrate solutions and water were used to test a sight glass and a differential pressure technique. The full-scale value for the sight glass is 55 in.

Survey of Production Facilities

Volume determination by direct observation of the liquid level of calibrated vessels is the most common means of volume determination for facilities with scrap recovery operations. The readouts for the liquid levels consist of calibrated sight tubes or calibrations marked on the transparent portion of a vessel. Tank capacities range from 14 to 2000 L, with SNM concentrations ranging from 0.02 to 250 mg/mL. Vessels are either columns, typically 5 in. in diameter, or shorter and wider containers filled with Raschig rings. Liquid level readabilities range from 0.05 to 0.5 cm; the large values tend to be used for volume determinations of low enriched uranium (LEU) solutions.

Calibration of these vessels is performed by the addition of increments of known volumes or masses of water as measured by calibrated weighing devices (gravimetric provers). In the latter case, the known density of the liquid at a particular temperature is used to convert mass into volume. Recalibration is usually performed on a regular basis with scheduled periods ranging from 5 months to 2 yr. Initial calibration runs involved 20 to 60 increments.

Data taken during calibration runs can be used to determine the random and systematic error of a volume measurement. Although replicate measurements could be used during multiple calibration runs to estimate random error, estimates were usually obtained by calculating the standard deviation of the data from the residuals of a fitted calibration curve. Linear calibration curves of the form $y = a + bx$ were used to fit the calibration data. Random errors ranged from 0.1% to 3.4%, with the majority ranging from 0.1% to 1.0%.

Systematic errors are calculated using the least-squares residuals from calibration curves by the methods descirbed by J. L. Jaech in Reference 4. The systematic errors estimated for tanks under routine production conditions are plotted in figure 3.21. Most systematic errors lie between 0.1% and 1.0% RSD.

Table 3.7 Summary of literature survey performance for sight glass systems

		Error (%)			
System	Readability	Random	Systematic	Total	Ref.
3-m (9.84-ft) long sight glass	1 mm (0.039 in.)	0.014[a] (0.007)[b]	— —	— —	29
1.4-m (4.59-ft) long sight glass	1 mm (0.039 in.)	0.10 [c]	0.05[c]	0.11[c]	22
0.767-m (2.52-ft) long sight glass	1 mm (0.039 in.)	0.54 [d]	0.18[d]	0.57[d]	33

[a] Percent full scale (9.84 ft), 1 σ.

[b] Standard deviation for measurement errors with the tank configuration error canceled out.

[c] Calculated from data in Ref. 22. Errors are for 1 σ, percent of full scale (4.59 ft).

[d] Percent full scale (2.52 ft), 1 σ. Errors are calculated from data.

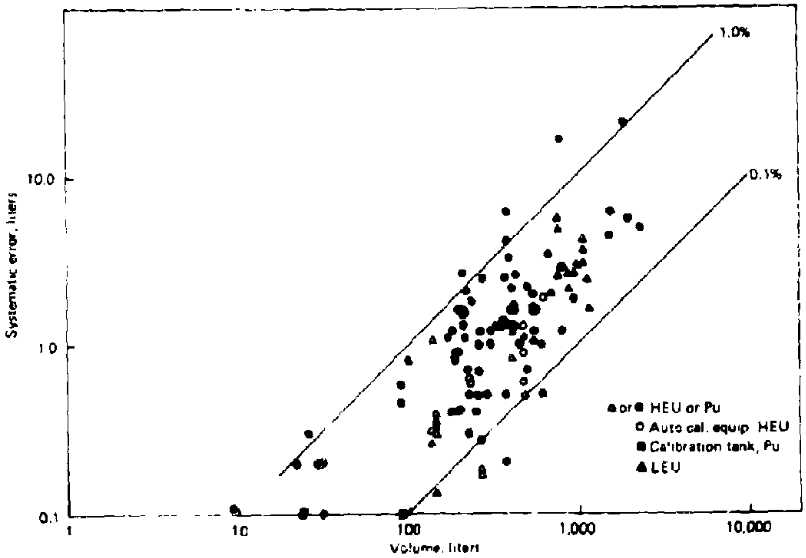


Figure 3.21 Systematic errors estimated for tanks in routine production use. (HEU = highly enriched uranium; LEU = low enriched uranium.)

3.3.1.3 Differential Pressure Methods

Description of Method

Differential pressure gauges (also called dip tube manometers or pneumatic bubblers) have historically been the accepted method for remotely measuring liquid level of radioactive solutions in process tanks in nuclear facilities (Ref. 34). The height of the liquid (of known or measured specific gravity) in the tank may be determined by measuring the difference in hydrostatic pressure between gas-purged probes in the tank. The hydrostatic pressure differential between a high-pressure (dip tube) probe located near the bottom of the tank and a low-pressure probe in the air space above the highest liquid level is defined by the expression

$$\Delta P = \varrho g h$$

where

ΔP = differential hydrostatic pressure
ϱ = density of the liquid
g = acceleration of gravity
h = distance between the tip of the liquid level probe and the surface of the liquid in the tank

A density probe can be installed in the liquid a known distance above the high-pressure liquid level probe. The differential hydrostatic pressure between these two probes can be related to the density ϱ of the liquid (Ref. 35) by

$$\varrho = \frac{\Delta P^*}{gh^*}$$

where

h^* = known distance between the tips of the density and liquid level probes
ΔP^* = hydrostatic pressure differential between the density and liquid level probes
g = acceleration of gravity

A schematic of a differential pressure system is shown in Figure 3.22. In the illustrated system, two lines go to a manometer for determining the height of the liquid in the process tank, and two more lines go to a manometer for determining the liquid density.

To measure the level of the liquid, the differential hydrostatic pressure measurements are made with a manometer or electromanometer. After corrections are made for the temperature of the manometer and the liquid in the tank, the liquid level is converted to volume using the calibration equation described in Section 3.3.1.1.

Scope of Applications

The differential pressure method can be used to measure any homogeneous liquid in the nuclear fuel cycle. It is especially useful when radiation levels require remote measurements. An additional advantage is that the output from the differential pressure systems can be used in remote control room operations or directly transmitted to computers. Like most liquid level measuring systems, the performance of the method will depend greatly on the configuration and regularity of the tank geometry.

Summary of Performance

A summary of the performance of several differential pressure gauges is presented in Table 3.8.

Equipment

The pressure difference between the dip tubes (probes) is measured with precision pressure gauges. Two dip tubes are required for liquid level measurements: a high-pressure dip tube extending almost to the bottom of the tank, and a low-pressure dip tube terminating above the highest liquid level in the tank. A third dip tube, with its opening located in the liquid and above the high-pressure dip tube, is used to measure the density of the liquid by measuring the differential pressure between the two immersed dip tubes with a precisely known vertical separation (Ref. 35). The separation of these tubes must be large enough to minimize error in the measurement, but small enough that the third dip tube always has its opening in the liquid. The minimum separation is between 7 (Ref. 29) and 10 (Ref. 26) in.

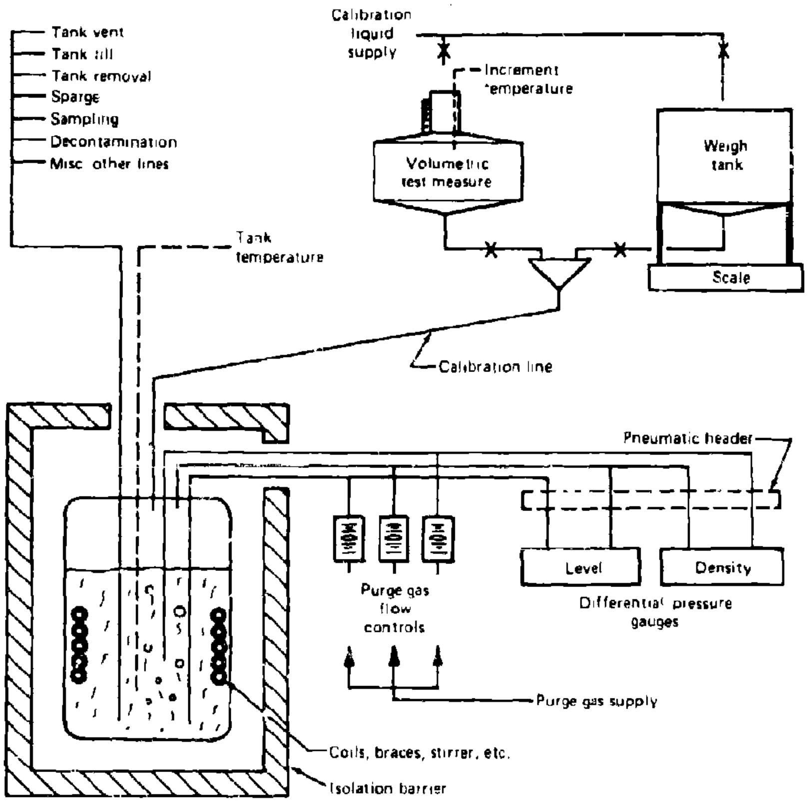


Figure 3.22 Schematic of instrumentation for the volume determination of liquid in a process tank by the differential pressure method.

The dip tubes are purged continuously with air or inert gas to permit pressure measurements and to prevent the entry of process solution and vapors into the tubes and back to the pressure gauges located in a nonradioactive area. Rotameters are adjusted to give equal flow of the purging gas to each dip tube.

Table 3.8 Summary of performance of differential pressure method[a]

Pressure Measurement System	Readability	Application Tank Volume	Performance (% RSD)	
			Random Error	Systematic Error
Water manometer, U-tube, 150-in.	0.1 in.	--	0.11	0.07
Water manometer, 100-in.	—	500 gal.	0.24	0.085
		1000 gal.	0.17	0.085
		2000 gal.	0.12	0.085
		5000 gal.	0.08	0.085
Oil manometer, 30-in.	—	500 gal.	0.85	0.35
		1000 gal.	0.65	0.35
		2000 gal.	0.45	0.35
		5000 gal.	0.27	0.35
Oil manometer, well-type	0.01 in.	2000 L	0.11	0.092
Hg U-tube manometer	—	90 L	0.10 to 0.22[b]	0.50 to 0.66[b]
Electromanometer	0.001 psi	300 L	0.015 to 0.017[c]	0.030 to 0.056[d]
		3000 L	0.011	0.038
Pneumatic pressure gauge		2000 L	0.096	0.04
			0.[illegible]	−0.4[e]

[a] Source of data for this table is literature survey except where noted by footnotes b.

[b] Source of data is the users' survey of production facilities.

[c] Based on residual analysis of data from 8 calibration runs.

[d] Based on slope and intercept variance from 8 independent calibration curves.

[e] Bias.

Differential pressure measurements can be made quite accurately with a conventional 150-in. manometer (Ref. 36). Manometers smaller than 150 in. may be easier to use because of their smaller size, but they may not provide the accuracy of the larger manometers.

Electronic pressure gauges operate by sensing the pressure difference with a transducer (e.g., a bellows or a spring) that generates an electrical signal proportional to the applied pressure. Two such instruments are discussed in the following paragraphs.

The electromanometer, shown in Figure 3.23, consists basically of two parts: a transducer and a servoamplifier. The transducer contains a bellows for pressure summing, a frictionless lever and linkage mechanisms to connect the bellows to an electromagnetic force coil, and a linear differential transformer. The servoamplifier acts on the error signal produced by the transducer when the linear differential transformer senses an unbalance caused by pressure applied to the bellows. In response to the error signal, the servoamplifier supplies a proportional signal to the transducer's force coil. This current results in an electromagnetic counterforce to the bellows precisely equal to the force arising from applied pressure. The amount of current flowing through the force coil is proportional to the magnitude of applied pressure.

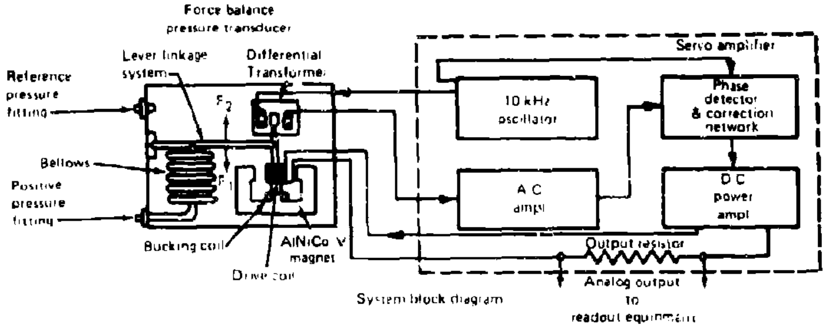


Figure 3.23 Schematic illustrating the principles of operation of electromanometer.

Another pressure gauge, shown in Figure 3.24, uses a quartz Bourdon tube as a transducer. The pressure sensor is comprised of a hollow helix quart Bourdon tube with two wire-wound coils suspended from it. These coils are positioned in a field of permanent magnets anchored to the body of the instrument. A curved mirror is welded to the Bourdon tube in such a way that it transmits any motion of the tube as a part of an optical lever. As test pressure is introduced into the Bourdon tube, the mirror translates a light beam to a pair of balanced photocells generating an off-null signal. This electrical current is amplified and fed through the force balancing coils, creating an electromagnetic torque equal to and opposite that caused by the pressure in the tube. This current is then passed through a precision resistor, creating an analog voltage directly proportional to the pressure in the system. Because of the high linearity of the servo loop, the results can be displayed on a digital voltmeter.

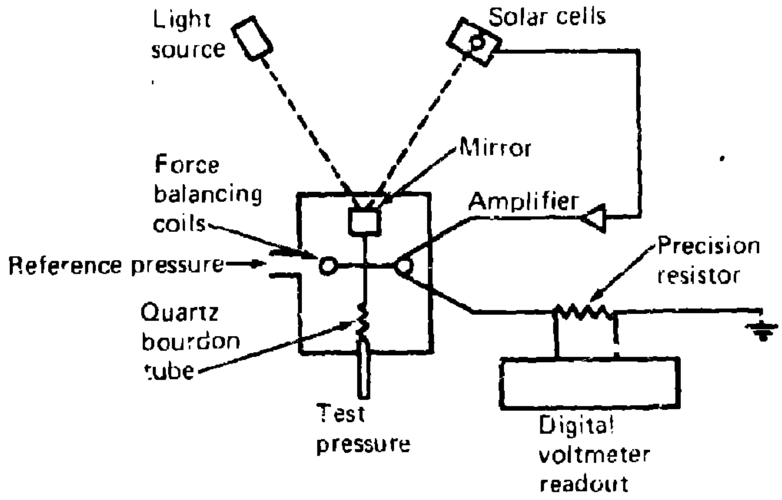


Figure 3.24 Schematic illustrating the principles of operation of a RUSKA pressure gauge (Model DDR 6000).

Major Sources of Error

Process tanks having smooth walls and the geometry of a right cylinder are ideal for measuring liquid volumes using differential pressure and other liquid level techniques. An ideal tank will have a calibration curve of liquid level vs volume as a straight line on which every calibration point falls. The errors associated with this calibration line, called systematic-type errors, reappear each time the calibration curve is used in making measurements.

Tanks having nonuniform geometries or internal obstructions such as piping and pipe supports are difficult to calibrate. Tanks with irregular geometry are treated as individual straight-wall sections stacked on top of one another, with the linear calibration curves for each section joined to each other at "joint points" (Ref. 34).

Other systematic-type errors result from the following:

(1) Unequal air purge flow rates in both dip tubes
(2) Nonlinearities and hysteresis
(3) Slow response times of meters and recorders
(4) Nonlinearities in the pressure transducer system

In a liquid U-tube manometer, the density of the fluid must be precisely known to determine pressure accurately. Because the density of the fluid may vary with temperature, it is important that the measurement of the temperature of the manometer be reliable. The temperature of the process solution, however, does not influence the manometer reading.

An operator's misreading of the scale, a common error, is more likely to occur with a liquid manometer using a finely graduated scale than with a digital electronic pressure gauge.

Small manometer fluid leaks can be compensated for by adjusting the tube or scale so that the reading under zero pressure differential remains at zero. Air leaks in the liquid manometer system, however, cannot be tolerated.

Measurement Control Requirements

The tanks to be used for SNM solution volume measurement should be drained, flushed, cleaned, inspected, and carefully recalibrated at least once a year. Calibration methods are summarized in Section 3.3.1.1. Detailed calibration procedures are also discussed in Refs. 20 and 21.

The pressure measurement instruments should be checked and/or calibrated frequently on a scheduled basis. Between tank calibrations, the tanks should be periodically flushed and cleaned to avoid sludge buildup and obstructions in the dip tubes.

Whenever possible, volume calibration checks should be performed either by adding a known volume to a tank and measuring the volume increase in the tank by differential pressure methods, or by comparing the volume measurements of a transferred solution in two or more tanks. The volume checks should be control charted and used as a guide for scheduling recalibration.

Data Analysis Requirements

It is more convenient to fit the calibration data to the calibration equation on a computer but it can be performed on a calculator.

Temperature and density corrections and conversion of the liquid level measurements to volume can be easily performed on a small calculator.

Survey of Selected Literature

Manometers, electromanometers, and pneumatic pressure transducers have been performance tested and used as pressure measuring instruments for differential pressure/volume measurement systems. The performance of the instruments is presented in Table 3.8. According to these reports, the electromanometers are nearly an order of magnitude better than either oil or water manometers. A pneumatic pressure transducer also yielded results superior to manometers except when a recorder output was used.

Electromanometer Systems

Three electromanometer differential pressure systems and an NBS sight glass were tested simultaneously by NBS (Ref. 29) and Brookhaven National Laboratory (BNL) (Ref. 31) on a 3000-L tank. The instruments tested were a Bell and Howell electromanometer, a RUSKA DDR 6000 pressure gauge, and a RUSKA XR−38 electromanometer. Eight independent calibration experiments were performed using standard volumes of water from a gravimetric prover. The calibration data from each experiment were fitted to a linear equation by the least-squares method. The systematic error (1 σ) was estimated from the variance of the calibration equation parameters for the eight calibration curves. The random error was computed from the least-squares residuals of all the calibration data. The results indicate no significant difference in the performance of the three electromanometers. A major source of error results from the tank geometry variations.

Pneumatic Pressure Gauge

A pneumatic pressure gauge (Nonlinear System, Inc., Model X−5) was tested at the Idaho Chemical Process Plant (Ref. 37) with a 2000-L accountability tank. Six separate calibration experiments were performed by adding increments of water from a prover. The calibration data from each experiment were fitted to a linear equation by the least-squares method. There was no significant variation in the estimated slope from run to run, but the intercept varied greatly because of variation in the discharge heel. A detailed analysis of error components is presented and the random and systematic errors are estimated.

A Foxboro pneumatic pressure gauge with output to a recorder was tested at Westinghouse Electric Corporation (Ref. 22). The performance of this instrument was poor compared to the system at the Idaho Chemical Process Plant. The random error was greater and the system exhibited a significant bias largely because of zero drift problems.

Manometers

A study to evaluate a 150-in. water manometer for measuring levels of water and uranium nitrate solutions in a 3000-gal. tank was conducted by General Electric Corporation (Ref. 26). The major source of error was believed to be due to large temperature variations in the manometer fluid (16°C to 42°C).

A 100-in. water manometer and a 30-in. oil manometer were tested using a 5000-gal. tank at Hanford Engineering Development Laboratory (Ref. 36). The performance of the 100-in. water manometer was similar to the result achieved with the 150-in. manometer at General Electric.

The performance of a 30-in. oil manometer was tested at the Idaho Chemical Process Plant on a 2000-L accountability tank (Ref. 37). Based on six calibration experiments, the performance of this well manometer was similar to the performance of the 100- and 150-in. water manometers previously discussed.

Tank Design for the Differential Pressure Method

A discussion of performance would not be complete without reference to tank design presently being used for differential pressure volume measurement. A representative example of a reprocessing tank may be found at the Barnwell Nuclear Reprocessing Plant. The 2150-gal. accountability tank in the high-level cell has a height of 11 ft and diameter of 6 ft. It has jacket cooling sized to cool contents from 171°F to 100°F using 76°F cooling water.

The dip tubes extending into such a tank may have diameters between 1/4 and 3/8 in. Stainless steel dip tubes, 1/2-in. in diameter, are used in the Hanford Reprocessing Plant (Ref. 38). The diameter of the dip tubes is a compromise between a larger opening, which would require a greater flow of purging gas to prevent the penetration of the corrosive liquid into the tube during the filling of the tank, and a smaller opening, which is subject to plugging.

It is desirable to have the lower dip tube extend as close to the bottom of the tank as possible without entering the sludge or causing interference with the flow of bubbles. At the proposed Exxon Nuclear Fuel Recovery and Recycling Center, the dip tube has been designed to extend to within 1/2 in. of the tank floor (Ref. 39).

A rotameter controls the flow rate of inert purge gas in a range from 0.1 (Ref. 20) to 0.5 ft^3/h (Ref. 38) Too rapid a flow of gas will create errors from the line friction. Too small a gas flow may allow liquid to enter the dip tube, especially while the process tank is being filled.

The separation distance between the upper density and lower liquid level dip tubes must be large enough to make the random error in the readout acceptable.

Survey of Production Facilities

Only one production facility visited had measurement control data on differential pressure volume measurement systems. A U-tube Hg manometer was used to measure the differential pressure on a set of three 5-in.-diameter tanks used to supply plutonium nitrate solution to ion exchange columns. There were two such systems which were calibrated with 20-L (gravimetric prover) increments of water.

3.3.1.4 Time Domain Reflectometry

Description of Method

Time domain reflectometry (TDR) is often referred to as a "closed loop radar" system (Ref. 40). The system operates by sending a voltage pulse down a transmission probe that is immersed in the liquid. When the pulse encounters any deviation in impedance (which includes the dielectric constant of the material), such as at the vapor/liquid interface, part of the incident pulse is reflected back to the sending point, where its trip time and its amplitude are compared with the original pulse. The relative amplitude of the received pulse is measured as the ratio of the amplitude of the reflected signal to the amplitude of the transmitted signal. This ratio, called the reflection coefficient, is a function of the dielectric constant of the coaxial line insulator. The reflection of the TDR probe may be displayed on a cathode ray tube (CRT) screen as a parameter in the y direction. A rapid change in slope along the x-axis corresponds to the vapor/liquid interface on the TDR probe. The location of the change in slope is used to obtain the liquid level in the tank.

After appropriate corrections for temperature and density, the liquid level in the tank is converted to volume using the calibration equation described in Section 3.3.1.1.

Scope of Applications

The TDR system can be used to measure the liquid level of all homogeneous SNM solutions in process, storage, or waste tanks. It is especially suitable where remote operations are desirable or are required by high radiation or control room operations. In addition, TDR can be used to measure the liquid level and the liquid/liquid interface level of two-phase systems (solvent extraction systems, for example).

The TDR system is attractive from a safeguards perspective because any tampering with the system (e.g., putting a hole in the outer conductor of the probe to give a false reading) can be easily identified. Advantages of the TDR system in a manufacturing plant are that it can be interfaced to a computer and that the TDR probe can be designed to give temperature, pressure, and liquid level measurements simultaneously (Refs. 34 and 41).

Summary of Performance

The performance of the TDR system is still being evaluated. Development of the system is being directed primarily toward providing a technique for safeguards inspectors to verify independently the liquid level in accountability tanks (Ref. 34). The performance of TDR systems reported in the literature is presented in Table 3.9. TDR systems were not observed during the survey of production facilities.

Table 3.9 Summary of performance for TDR systems[a]

Performance Test	Liquid Level Evaluated (m)	Performance (% RSD)	
		Random Error	Systematic Error
Test runs conducted with ordinary tap water, nitric acid, and dilute uranium solutions	2	0.1	—
Test runs conducted with nitric acid	0.193	5	2.6

[a] L = Literature survey.

Equipment

A vertical, partially sectioned view of the TDR probe is shown in Figure 3.25 (Ref. 42). This probe has a central cylindrical conductor surrounded by a coaxial cylindrical conductive screen. Both cylinders are made of stainless steel. The screen is perforated to allow the liquid under examination to circulate freely inside the probe (i.e., between the central conductor and the screen).

The central conductor of the probe is centered by a ring made of insulating material, such as polyethylene, which also ensures a perfect liquid and gas seal. The conductor centering is maintained in the lower part by a stainless steel perforated ring, which, at the same time, also creates a short circuit at the probe end. The plug is provided with a crown of equally spaced vertical holes, which allow the free circulation of liquids in and out of the probe. The measuring probe is connected to the electronics and to the display installation by a coaxial cable with low capacity and attenuation.

The electronic components associated with the TDR system are (1) a sampling device to measure the input signals and to send the driving voltages to the display unit, (2) a pulse generator to transmit pulses to the probe, and (3) a display unit, which can be either an oscilloscope or an x-y recorder.

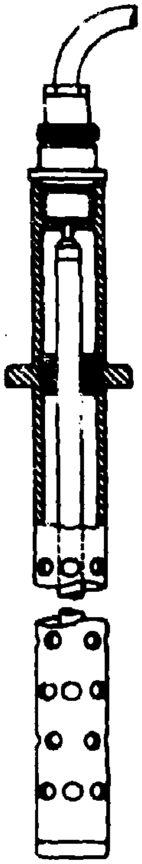


Figure 3.25 Typical TDR probe for liquid level measurements (Ref. 42).

A typical TDR installation suitable for use in a plant is shown in Figure 3.26. The equipment shown is an x-y recorder, oscilloscope, pulse generator, and pulse sampler to measure the received pulse. Examples are given of readouts for tanks containing liquids with one, two, and three interfaces corresponding to *A*, *B*, and *C*, respectively, in Figure 3.26.

Major Sources of Error

A major source of error for the TDR system, in common with such other liquid level techniques as the differential pressure gauge and sight glass, is the geometry of the process tank and the deviations in the tank walls from a perfect right cylinder. The proper geometry for minimizing volume measurement errors favors a high length-to-diameter ratio.

Additional sources of error related directly to the TDR system are associated with the pulse rise time of the signal transmitted down the probe. The pulse rise time is the time the pulse takes to reach its maximum height. A short rise time permits a greater resolution. Degradation of the signal and loss of resolution can result from excessively long cable lengths between the probe and the electronics. Spurious electrical signals may cause drift in the as-received, reflected signal. These can be attenuated by the use of filters and shielding.

Measurement Control Requirements

The tanks should be drained, cleaned, inspected, and recalibrated at least once a year. Several calibration runs should be performed while the tank is out of service. Calibration procedures are described in Refs. 20 and 21 and are summarized in Section 3.3.1.1.

The tanks should be flushed and cleaned from time to time during routine operations to avoid sludge accumulation. Each time a volume increment is transferred to another tank, the decrease in the volume of the first tank should be compared with the volume increase in the second tank. The values should be charted for control and monitoring. If values remain within statistical limits, it may not be necessary to recalibrate as frequently as was suggested.

Data Analysis Requirements

The least-squares fitting of calibration data is more conveniently performed by a computer but can be performed with a small calculator. Temperature corrections and the conversion of liquid level to volume can be made easily with a small calculator.

Survey of Selected Literature

The performance results for the TDR system are summarized in Table 3.9. At BDM Corporation, a specially designed combination TDR/differential pressure probe was tested with water, dilute nitric acid, and dilute uranium trioxide solution (Ref. 41). This special probe permitted simultaneous measurements of liquid level and liquid density. A measurement error for a vessel possessing a liquid height of 6 ft was stated as being approximately 0.1%. However, no data, discussion, or error analysis was presented.

The results of a test in a nitric acid solution for a maximum liquid level of 193 mm (Ref. 42) are given in Table 3.9. The random error was estimated from the standard deviation of the residuals, and the systematic error was estimated from the error in the calibration equation for a liquid level of 193 mm.

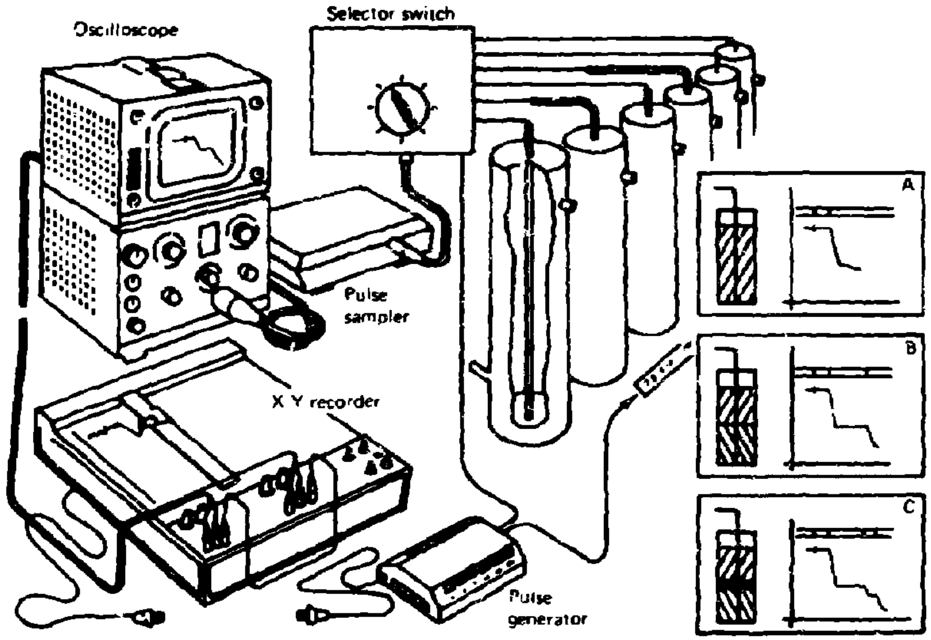


Figure 3.26 Equipment installation for TDR, typical plant operation (Ref. 42). Inserts *A*, *B*, and *C* are examples of readouts for tanks containing liquids with one, two, and three interfaces, respectively.

3.3.1.5 Miscellaneous Liquid Level Techniques

A brief description of several other types of liquid level gauges for which performance data are not available is given in the following paragraphs.

3.3.1.5.1 Conductivity Probe

The conductivity probe measures the liquid level by means of resistive transducers. The resistance between two electrodes or between one electrode and the grounded tank wall is related to the level of conductive liquid in the tank. As more electrode surface is immersed in the liquid, the resistance between the electrodes is reduced. The control unit supplies a sensing current sufficiently small to avoid causing electrolysis or a potential explosion hazard.

3.3.1.5.2 Inductivity Coil

The inductivity coil senses the liquid level when the liquid enters the hollow tube that is the core of an induction tube coil. The tube is wound with the primary and secondary windings of the coil. As the liquid enters the core of the induction coil, the permeability of the core increases relative to air, and there is a corresponding increase in current induced in the secondary winding. The tube must be of a material with a low relative permeability coefficient to distinguish between the fluid and unfilled tube.

3.3.1.5.3 Resistance-Wire Elements

Resistance-wire elements, which are enclosed in an open tube and heated, change their electrical resistance as liquid comes in contact with them and changes the transfer of heat from the elements.

The operating temperature of the wire, for a given power, is a function of the heat transfer coefficient between the wire and the ambient fluid. To improve response time, as much wire surface as is practical is exposed to the ambient fluid. This technique suffers from the problems associated with oxidation and corrosion of the resistance element.

3.3.1.5.4 Ultrasonic Gauge

An ultrasonic gauge can sense the liquid level in the process tank in several ways, depending on the orientation used for the ultrasonic transmitter and receiver. The basic principle of the ultrasonic gauge is that an ultrasonic wave may travel in a liquid or solid with relatively small attenuation compared with its travel in air. In one orientation the transmitter and receiver face each other across the diameter of a tank, producing a single point measurement. When the liquid level rises just high enough to immerse both crystals, the ultrasonic transmitting signal will be detected by the receiver.

For a multipoint measurement of the liquid level, a measuring station (pair of crystals) or a series of measuring stations is vertically aligned along the tank axis at known heights so that the rise or fall of liquid in the tank can be monitored.

For continuous liquid level measurement, the transmitter and receiver may be fastened to the bottom of the tank so that the transmitted signal will be reflected at the liquid surface. The path length for the ultrasonic signal will change with the height of the liquid level. The change in path length corresponds to a delay in time for the transmitted signal to reach the receiver. This delay can be measured and converted to length using the speed of sound in the solution and the actual path the sound travels. The ultrasonic sensors are simple, easy to mount, durable, and not sensitive to gamma radiation. The number of measuring stations that can be monitored by a single electronic package is quite large.

3.3.1.5.5 Capacitive Continuous-Level Transducers

Capacitive continuous-level transducers use either a single probe, two or four concentric cylinders, or special electrode shapes. Capacitive level probes have been built in lengths exceeding 10 m (32.8 ft). The capacitive elements can be contoured to match the tank geometry.

3.3.2 Chemical and Isotopic Dilution Methods

Description of Method

When a known amount of a chemical or isotope tracer is dissolved in an unknown volume of liquid, the resulting concentration of the tracer in the liquid is inversely proportional to the volume of the liquid. These methods of volume determination are called chemical and isotopic dilution techniques.

In practice (Refs. 24, 43, and 44), the tracer is usually in the form of a solution whose concentration is very accurately known. An accurate aliquot of the tracer solution is added to a process tank, and the liquid in the tank is thoroughly mixed to give a homogeneous solution. The liquid in the tank is then sampled and analyzed for the tracer concentration by chemical, isotopic, or radiometric methods.

The volume is then calculated using the equation

$$V_{\mathrm{tank}} = \frac{V^{\circ}_{\mathrm{tracer}} C^{\circ}_{\mathrm{tracer}}}{C_{\mathrm{tank}}} \qquad (3\text{-}9)$$

where

V_{tank} = volume of liquid in the tank

$V^{\circ}_{\text{tracer}}$ = volume of tracer solution added to the tank
$C^{\circ}_{\text{tracer}}$ = concentration of the tracer solution
C_{tank} = concentration of tracer in the tank solution

There are several limitations of the chemical and isotopic tracer dilution techniques. A major difficulty is that the tank construction in most operating reprocessing plants makes it difficult to quantitatively transfer the small volume of tracer solution into the tank. Another difficulty is in finding a tracer that is compatible with the reprocessing chemistry and can be measured easily and accurately by chemical, isotopic, or radiometric techniques. If the tracer is not compatible with the processing chemistry, it must be subsequently removed from the solution before further processing.

Several tracers have been considered. Magnesium and zinc are inexpensive and can be spectrometrically analyzed to fairly high accuracies—magnesium to 0.2% to 0.3% (Ref. 43) and zinc to 0.5% (Ref. 40). Lithium is also inexpensive and obtainable in high purity (Ref. 44), it presents many problems in determining its isotopic composition accurately (Ref. 43).

Although it is very expensive, rhenium can be analyzed at very low concentration levels and, therefore, may be used in much smaller quantities than the other tracer elements (Ref. 40). Theoretically, this strategy should facilitate obtaining a more accurate analysis; however, by using smaller quantities of an element, other factors can alter the concentration of the tracer element in the solution and cause significant error. For instance, adsorption of the element on solid surfaces has a greater impact on the total error when the nanogram-per-milliliter level (Ref. 40) is used for rhenium additions.

Scope of Applications

The chemical and isotopic dilution method can be used when a tracer can be found that does not interfere with downstream processing goals, is not present in the liquid to be measured, and can be accurately analyzed at very low concentrations. Although it is unlikely that this method will be used routinely for volume measurement, it may be the best method for measuring the heel volumes of process tanks and for other applications when more convenient methods are not applicable or appropriate. It could also be used as an independent method for inspectors to verify tank volume calibrations.

Summary of Performance

A summary of the performance of chemical and isotopic dilution techniques reported in the literature for measuring the volume of liquid in process tanks is given in Table 3.10. This method was not observed during the survey of production facilities.

Table 3.10 Summary of performance for chemical and isotopic dilution techniques for measuring solution volume

	Systematic Error (%)	Total Error (%)	Ref.[a]
Mg tracer	—	0.34[b]	43
^{6}Li/^{7}Li system	—	0.31[c]	44
Zn tracer	0.3 to 0.9	0.33[d]	40

[a] Literature Surveys.
[b] Percent difference in volume from weighing technique.
[c] Percent difference in measured volume from actual volume.
[d] Percent difference from volume measured by differential pressure technique.

Equipment

The major equipment required for this method is used for analyzing the tracer. The selection of this equipment depends on the tracer used and on the analytical methods selected. Other equipment required includes the volume or mass measurement equipment necessary for aliquoting the tracer into the tank.

Major Sources of Error

The major sources of error include:

(1) Error in the concentration of the tracer solution
(2) Error in the volume or mass of tracer solution added to the tank
(3) Sampling error as a result of insufficient mixing in the tank
(4) Errors in tracer concentration in process solution prior to spike
(5) Errors in tracer analysis of process solution after spike
(6) Adsorption of tracer spike on tank surfaces or solids in the tank
(7) Interference of impurities in process solution with tracer analysis

Measurement Control Requirements

The analytical methods used to assay the tracer concentration in the tracer solution and in the process solutions will require measurement control programs, including calibration with tracer standards traceable to the national measurement systems, resolution of the standard to sample differences on method performance, and the use of frequent analytical check standards, to ensure that calibration data reflect the quality of measurements. These measurement control procedures will depend on the tracer and analytical methods used.

Data Analysis Requirements

The data analysis requirements for calculating tracer concentrations will depend on the tracer and analytical methods selected. The calculation of tank volume, given the concentration of tracer solution, the volume of tracer solution added, and the concentration of tracer in the process solution, is simple and can be conveniently performed on a pocket or desk calculator.

Survey of Selected Literature

The total errors for three different isotopic dilution techniques are given in Table 3.10.

The analysis performed at the Bhabha Atomic Research Centre, Bombay, India, used accountability tanks filled with up to 1510 kg of demineralized water (Ref. 43). The magnesium tracer solution was added through a 1/2-in. stainless steel line that led from the operating gallery outside the cell into the tank. The isotope ratios were measured with a Varian MAT CM−5 mass spectometer. Volume measurements using the differential pressure technique and direct weighing were compared with the values from the isotopic dilution technique. The errors of these methods were found to be approximately the same.

The results reported for the work performed by Bokelund (Ref. 44) were for small (50 to 200 mL) volumes of a simulated process solution. The reported error was obtained from six runs in which the percent difference is between the volumes measured by the isotopic dilution technique and the "rated" volume.

The work by Nentwich (Ref. 40) was performed using mockups of processing tanks and 350 to 550 L of demineralized water slightly acidified with nitric acid. A number of samples were taken at the same level in the tank and the volume measurements using the isotopic dilution method and differential pressure method were compared.

3.4 FLOW MEASUREMENTS

Description of Method

Flow of a liquid or a gas can be measured by flowmeters classified into two categories (Ref. 45):

(1) Quantity meters
    (a) Piston
    (b) Nutating disk

- (c) Rotary vane
- (d) Metering pump
- (2) Flow rate meters
  - (a) Variable head meters
    - (i) Orifice
    - (ii) Venturi tube
    - (iii) Pitot tube
    - (iv) Flow nozzle
    - (v) Changing area
  - (b) Variable area meters
    - (i) Rotameter
    - (ii Flow drag force
    - (iii) Airlift
    - (iv) Ejector
  - (c) Velocity and current meters
    - (i) Turbine
    - (ii) Thermal
    - (iii) Laser-beam-doppler effect
    - (iv) Nuclear magnetic resonance
    - (v) Electromagnetic
    - (vi) Vortex
    - (vii) Ultrasonic

The quantity meters measure fluid flow by separating the stream of fluid into discrete, isolated quantities of precisely known mass or volume increments. The number of these quantities is counted to determine the quantity of fluid that passes through the meter. Meters falling into this category are described in Ref. 46. Rate meters measure the rate of flow of a fluid in a continuous stream. Integration of this measurement with time is necessary for obtaining the total amount of fluid passing through the meter. For a discussion of the principles of operation of these flowmeters, see Ref. 47.

Scope of Applications

In the nuclear fuel cycle, flow s are used most commonly for process control applications, rather than for applications associated with MC&A, because of their low accuracy relative to mass and volume measurement methods. When used in conjunction with other measurement methods, however, flow measurements may be suitable for certain safeguards applications.

Flow measurements of liquids are often used in fuel processing plants for process control of liquid extraction columns (for example, adding chemical solutions to solvent purification systems and liquid transfers between tanks). In fuel fabrication plants and gaseous diffusion plants, flowmeters are used for the measurement of UF_6. In general, appropriate applications may exist where the required precision is between 1% and 5%.

Rotameter-type flowmeters (Ref. 48) are used for metering extraction-column feeds from tanks in the canyon of the Hanford reprocessing plant where the large production equipment is located. They are also used in conjunction with a pneumatic controller for controlling the flow rate in the process stream. By means of a solenoid valve and control valve, the rotameter can prevent reverse drainage to the feed tank. A schematic in Figure 3.27 illustrates how a rotameter located in a "hot" area is used. In hot areas inaccessible to maintenance activities, electronic rotameters with an electric pneumatic converter for the controller/recorder are used. In cold areas where maintenance is easier, pneumatic rotameters that do not require the converter may be installed.

The most accurate technique for measuring the rate of flow is monitoring the rate of change of the level of liquid in a tank. Liquid level techniques have been discussed previously. Where these are not suitable, continuous flow measuring instruments with lower accuracies may be used.

The highest accuracies are generally obtained with quantity type flowmeters, specifically, positive displacement-type flowmeters, which are the most suitable for nuclear applications. The quantity meters are actually pumps with registers and do not permit unrestricted flow in a system. Liquids and gases subject to thermal and pressure effects on their volumes require appropriate correction factors. Another consideration is the effect of the corrosiveness of the liquid on the life of the seals in the meter.

Variable head flowmeters, which use a restriction of the flow path to generate a pressure head, are simple in principle, but they are subject to frequent maintenance because of erosion or plugging of holes in the orifice plate, venturi tube, pitot tube, or flow nozzle. Any change in the cross section through which the fluid flows will alter the calibration and create an error in the measurement.

Velocity and current meters have no history of use in radioactive service but have several potential advantages. The turbine flowmeter can be very accurate, although in a corrosive or a nonlubricating environment, protection and maintenance of the bearings to prolong life become significant considerations.

Flowmeters using an ultrasonic signal have the advantage of being external to the flow stream so that severe environmental problems are eliminated and any maintenance can be performed without major disruptions to the process line. Ultrasonic flowmeters have been reported with accuracies of 0.3% (Ref. 49) but can be adversely affected by entrained air, which may cause bubbles to form in the liquid stream.

The electromagnetic flowmeter, which operates on the principle of a dynamo with the rotor replaced by the flow of the fluid, can only be used for fluids with sufficient electrical conductivity, particularly liquid metals. The flow of aqueous and organic solutions in a reprocessing plant cannot be measured by this technique because they do not have sufficient conductivity.

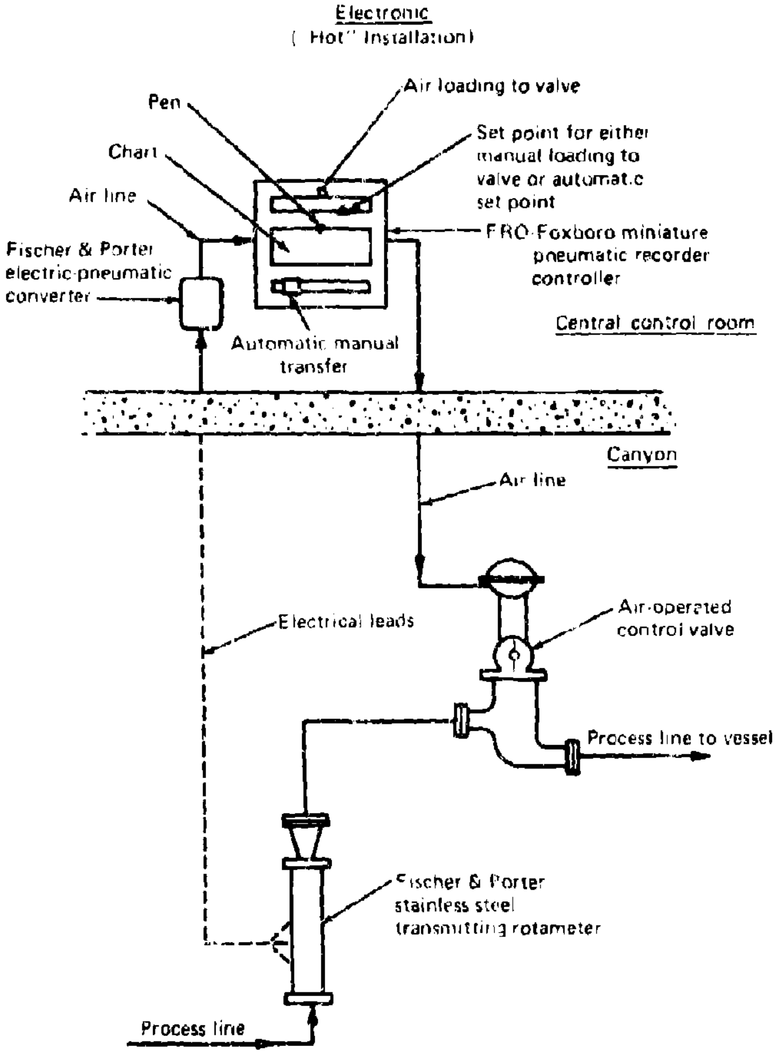


Figure 3.27 Rotameter systems (Ref. 48).

Summary of Performance

A summary of performance of flowmeters that may have potential applications in the nuclear industry is tabulated in Table 3.11.

Equipment

The flowmeter instruments described in this section are those in use in the nuclear industry (Ref. 48). The choice of systems depends on the accuracy of measurement desired, the flow rates, and the range of flow rates likely to be encountered.

Electronic Rotameter (Ref. 48)

A specially designed (Fischer and Porter) all stainless steel electronic rotameter is used to measure the flow of most radioactive streams within the Hanford Purex Plant for large tanks and other reprocessing equipment for storage. Figure 3.28 is a cross section of this rotameter. Rotameters use a constant differential head across a variable annular restriction to measure the flow rate of a fluid. The stream being measured passes upward through a vertical, truncated cone metering tube having the maximum diameter at the top. A float inside the tube adjusts its vertical position as required by the flow rate and in so doing changes the annular area between the tube and the maximum diameter of the float.

The weight of the float is compensated for by a loss of momentum of the streaming liquid, which enters at the bottom of the conical metering tube and exits along the rim of the float. The instrument is calibrated by recording the position of the floating element for a known volume flow rate of a liquid with a known specific gravity:

$$F_b = F_a \sqrt{\frac{\varrho_a}{\varrho_b}} \qquad (3\text{–}10)$$

where

F_a = the volume rate of flow for liquid *a* (calibration)
F_b = the volume rate of flow for liquid *b*
ϱ_a = the specific gravity of liquid *a*
ϱ_b = the specific gravity of liquid *b*

Electronic rotameters have an armature consisting of a vertical stainless steel tube, the lower half of which is filled with a soft iron core attached to the bottom of the float. The armature moves inside two coils, as shown in Figure 3.28. As the flow area increases, both the float and the armature rise, changing the inductances of the two coils and generating a signal that is transmitted to a recording device.

Table 3.11 Summary of performance of flowmeters applicable to nuclear facilities[a]

Type	Accuracy (%)	Sensitivity (%)	Comments
Positive displacement:			
Piston Nutating disk Rotary vane	0.2 to 1	1	Not used in radioactive service because of moving parts in process streams and problems with solids and bearings; good accuracy over wide range of flow rates; useful for cold chemical feeds.
Metering pump	0.5 to 1	2	Primarily a fluid-transfer device; poor for handling solids; high maintenance and complexity; useful for cold chemical feed makeup.
Variable head meters:			
Orifice	0.5 to 2	2	Require penetration of pipe wall and internal line restriction; high permanent pressure loss; require local transmitter or sensing lines to external area; sensing lines and diaphragm seals must be accessible for servicing; solids may erode or plug primary elements.
Venturi	1	—	
Pitot	1 to 3	—	
Variable area meters:			
Rotameter	0.5 to 2	2	Tapered-tube metallic unit with magnetic follower and electronic transmitter is used in radioactive service; float partially obstructs flow; constant pressure drop.
Piston (plugged and ported) cylinder	0.5 to 2	—	Similar to rotameter; tight clearances between plug and cylinder may be a problem when handling fluids containing solids; no known application to radioactive service.

Note—See footnote at end of table.

Table 3.11 Summary of performance of flowmeters applicable to nuclear facilities[a] (Cont'd)

Type	Accuracy (%)	Sensitivity (%)	Comments
Airlift	3 to 10	—	Simple and reliable; flow rate is correlated with rate of air flow to lift (rotameter); no control or elements located in process area; commonly used for radioactive fluid transfer.
Ejector	5 to 20	—	See airlift comments.
Velocity and current:			
Turbine	0.25 to 1	0.25	Commonly used for hydrocarbon metering and accounting; has moving parts and bearings in fluid stream; solids and nonlubricating streams may present problems.
Vortex	0.25 to 1	—	Good accuracy; has rotating element in fluid; can reportedly be used in nonlubricating fuid; no known application in radioactive service.
Thermal	2	—	Primarily for low flow rates.
Electromagnetic	1	0.25	Commonly used in radioactive service; no moving parts or obstructions in pipe; low maintenance; requires conductive fluid.
Ultrasonic	0.1 to 1	—	Good accuracy and precision; generally limited to pipe diameters of < 4 cm; limited experience in plant usage.

[a] Sources: Refs. 45, 47, 48, and 50.

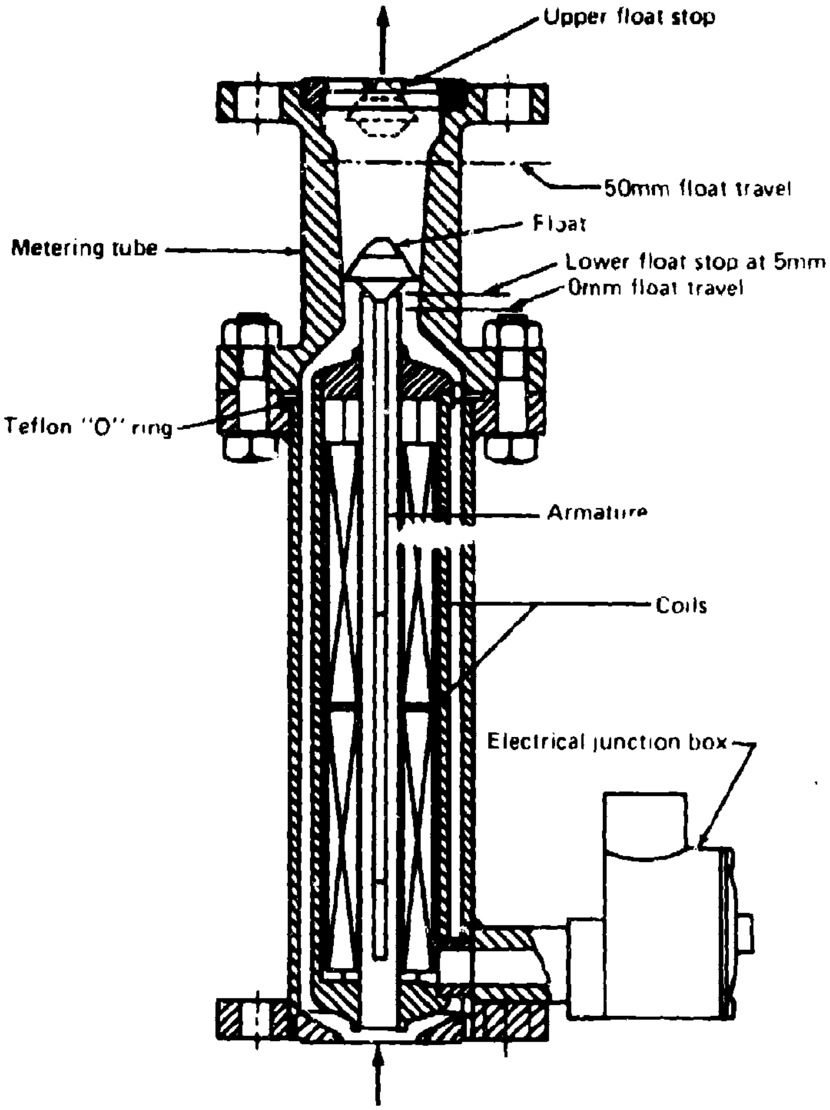


Figure 3.28 Electronic rotameter (Ref. 48).

Pneumatic Rotameter (Ref. 48)

The pneumatic transmitting rotameter is used mainly to measure the flow rate of "cold" process streams.

The principle of operation is the same as for the electronic rotameter, except for the method of transmission of the signal. The difference is that as the armature in Figure 3.28 moves, a pair of external magnets follows, and through a mechanical linkage system, operates a pneumatic transmitter to give an air signal proportional to the float position.

Orifice Meters (Ref. 48)

The orifice meter system is used chiefly for stream and water flow measurements, but can also be used to measure the flow of radioactive off-gas streams.

Orifice meters operate on the principle of constant-area flow restriction with variable head (pressure) loss. The liquid passing through the orifice increases velocity. The kinetic energy gained by the liquid results in a decrease in pressure after the orifice (P_2) compared with the pressure before the orifice (P_1).

The pressure difference ($P_2 - P_1$) between points before and after the orifice is proportional to the flow rate of liquid through the orifice, F, and the density of the liquid, ϱ:

$$F = K_1 \sqrt{\frac{P_2 - P_1}{\varrho}} \tag{3-11}$$

The flow meter, shown in Figure 3.29, is a circular hole in a thin, flat plate that is clamped between the flanges at a joint in the pipeline so that its plane is perpendicular to the axis of the pipe and the hole is concentric with the pipe. A differential pressure gauge is connected to side holes in the pipe wall on both sides of the plate so that the difference in fluid pressure ($P_2 - P_1$) on both sides of the orifice can be measured.

A "head-above-orifice" flowmeter, also called a flow pot, is shown in Figure 3.29. The flow pot operates when a chamber begins to fill with an entering liquid that can leave only through an orifice in the chamber wall. The level of liquid in the chamber is measured with a differential pressure gauge. It rises until the hydrostatic head above the exit orifice is high enough to cause an exit flow equal to the entering flow. The steady state liquid level, as measured by the differential pressure gauge in the chamber, is a measure of the flow rate.

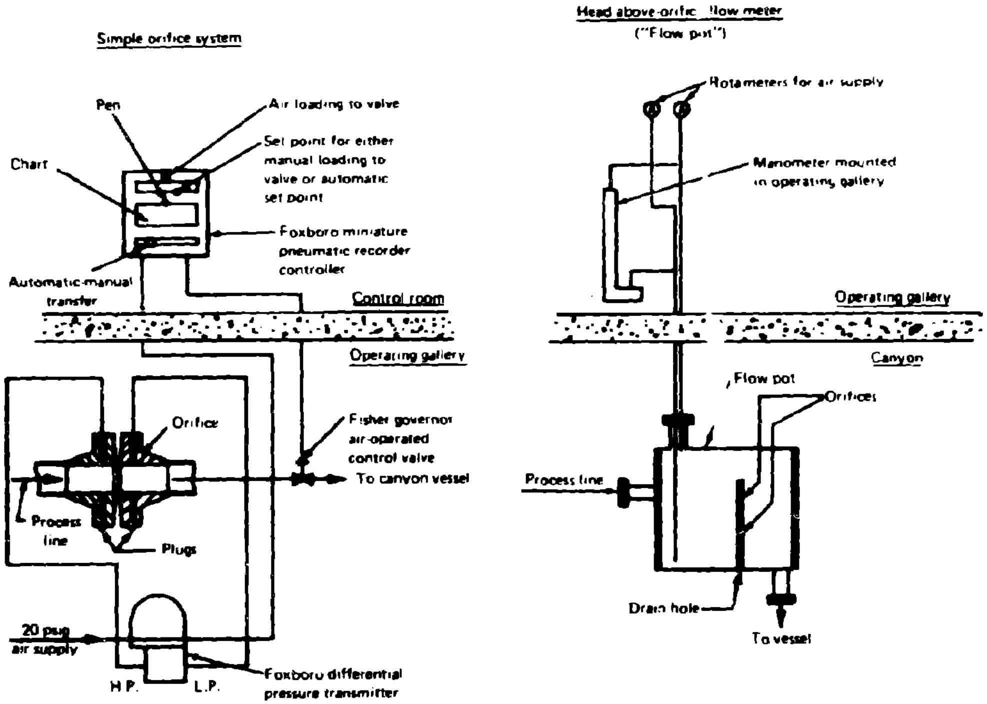


Figure 3.29 Orifice systems (Ref. 48).

Metering Pumps (Ref. 48)

Metering pumps use a reciprocating piston having an adjustable stroke and/or frequency to provide positive displacement of the liquid.

"Milton Roy" metering pumps are often used in "cold" process streams for continuous maximum flow rates less than 0.2 gal./min.

Displacement Meters (Ref. 48)

Displacement meters are used to measure the volume of process streams for batch transfer of the solution in those cases where it is desirable to know the volume transferred.

The displacement meter contains a reciprocating piston that is activated by the passage of a fixed volume of liquid. The reciprocating piston, through a gear train, activates a counter and registers total flow.

Electromagnetic Flowmeter (Ref. 47)

The electromagnetic flowmeter consists of a pipe and a means of establishing a magnetic field transverse to the pipe. The pipe is either nonconductive or lined with an insulator. If a fluid is sent through such a device, an electric field appears in the moving fluid perpendicular to both the magnetic field and the fluid velocity vector. The electric field is usually detected as the potential difference between two electrodes in contact with the fluid but insulated from the pipe. The induced electric potential is proportional to the average fluid velocity through the pipe. The electrodes can also be arranged on the surface of nonconductive (dielectric) pipe, as shown in Figure 3.30. This arrangement excludes direct contact of electrodes with the flowing liquid. This type of flowmeter is presently used in e new types of fuel reprocessing plants.

Ultrasonic Flowmeter (Ref. 51)

The time differential clamp-on ultrasonic flowmeter transmits an ultrasonic beam between two transducers clamped to opposite sides of an exiting pipe at a known angle relative to the flow. (See Figure 3.31.)

The rate of flow of liquid V_f through a pipe is expressed by

$$V_f = \frac{V_s \Delta T_s}{T_s \sin \theta} \tag{3-12}$$

where

V_s = velocity of sound in the liquid being measured
ΔT_s = time difference between the arrival of a signal from A with and without liquid flow ($\approx 10^{-12}$ s)

T_s = time of passage of a signal from A to B without flow (10 to 20 μs)

θ = angle between a perpendicular to the pipe surface and a line joining the two transducers; $\theta = 30°$ for a 1-in. pipe

Another type of ultrasonic flowmeter, the transit time flowmeter, functions by measuring the transit time of a small bubble with ultrasonic detectors mounted outside of the pipe. At the Idaho National Engineering Laboratory (Ref. 49), a transit time flowmeter unit was fabricated and after testing was found to have a 0.3% accuracy.

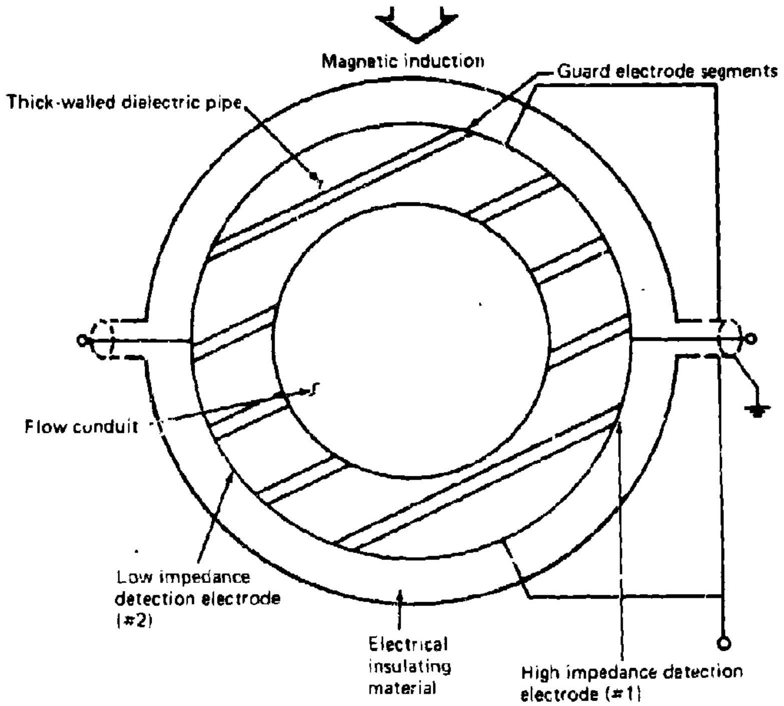


Figure 3.30 Schematic of electromagnetic flowmeter with detection electrodes on exterior surface of dielectric pipe (Ref. 47).

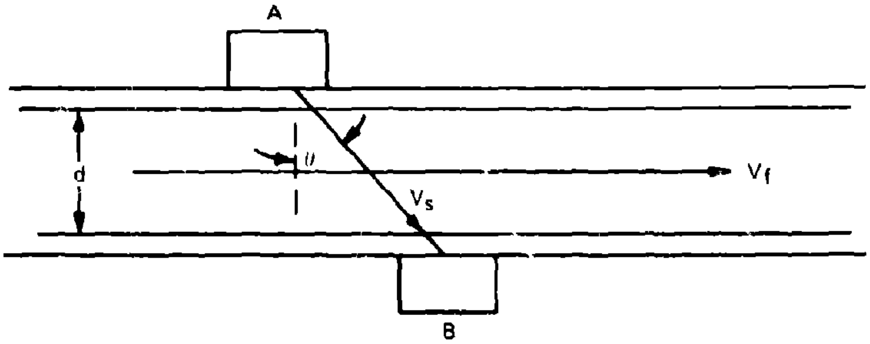


Figure 3.31 Principle of time differential ultrasonic flowmeter (Ref. 49). (*A* = upstream ultrasonic receiver and transmitter; *B* = downstream ultrasonic receiver and transmitter.)

Laser-Doppler Anemometer (Ref. 51)

A laser-doppler anemometer operates with two crossed laser beams. The beams are brought to a focus with an angle at the crossing point where the velocity measurement is made. A photomultiplier tube on the opposite side of a transparent pipe or duct detects light scattered from particles in the measuring volume. These particles have an instantaneous particle velocity u given by the equation

$$u = \left(\frac{\lambda f_D}{2 \sin(\theta/2)}\right) \pi r^2 \qquad (3\text{-}13)$$

where

λ = wavelength of the laser radiation
f_D = doppler frequency shift caused by the movement of the scattering particle
θ = angle between the two laser beams

The accuracy of a velocity measurement thus hinges on measurement of a doppler frequency. This light frequency shift results from scattered light caused by the moving particle. This flowmeter requires little calibration, but transparent pipe has to be used in the flow measuring region.

Major Sources of Error

The flowmeter methods generally exhibit low precision—usually 1% to 3% of the total volume of delivered liquid or gas. The imprecision is caused by three sources of error: (1) the nonhomogeneous velocity distribution of flow in a pipe, (2) the lower sensitivity to flow variation, and (3) the necessity to integrate precisely the variable flow rate over a long period of time and over the cross section of a pipe. Some modern flowmeters could reach a precision of 0.25% for constant flow under some equilibrium conditions. However, the average flow rate has to be obtained by integration from the fractional flow rates in each particular cross section of measured pipe or duct. Some sensors can do this averaging directly; others, for example, the laser-beam-doppler flowmeter, have to be aided by mathematical averaging with a computer.

Only the flowmeters with reciprocating pistons, rotary pistons, sliding vanes, or lobes could approach 0.2% precision. All the flowmeters used in the Hanford Purex Plant have a precision of 2% to 3%.

Measurement Control Requirements

Flowmeters have to be calibrated by the same methods used for calibrating tanks, that is, by flowing a weighed amount of liquid or a precisely measured volume of liquid at a constant rate of flow, and recording the temperature, density of the liquid, and its flow rate (measured simultaneously by the volumetric method). From these calibration data, the calibration curves may be constructed. For an accurate interpretation of the flowmeter readings, these calibration curves should be used under the same conditions that existed during calibration. This means that the same temperature, density, pressure, and time of measurement used in the calibration runs must be used in production runs to eliminate the need for correction factors.

Data Analysis Requirements

The quantity-type flowmeters, such as the piston meter, usually have registers (Ref. 46) that integrate the flow rate over the period of time the meter is operating to give the volume of liquid transferred. To obtain the total volume from flow rate meters, the average flow rate must be multiplied by the time. These calculations and the calibration calculations are simple and can be performed on a desk calculator.

Survey of Selected Literature

The use of flowmeters in the nuclear industry for material safeguards is very limited, and published data for this application are not readily available. A summary of the performance of the different types of flowmeters used mostly for nonnuclear applications is given in Table 3.11.

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CHAPTER 4

Chemical Assay Methods

4.1 INTRODUCTION

This chapter presents a critical review of chemical methods for determining the concentration and isotopic composition of uranium and plutonium. Because there are literally thousands of published methods, it was necessary for us to be selective and to include only those methods we deemed to be of primary importance and utility. The fact that a method or procedure is not included does not mean that it may not be useful. We have included only those methods readily available in the open literature. Unless a publication was available in English or in a language that we, the authors, were able to read, it was not included.

For the determination of total special nuclear material (SNM) in a lot or batch, both the concentration of SNM and the bulk weight or volume of the lot or batch must be known. Prior to chemical analysis, a representative sample must be obtained. The error in determining the quantity of SNM is a combination of the bulk measurement error, sampling error, and analytical errors.

The analysis of radioactive samples that may contain Th, U, Pu, higher actinides, and fission products presents special problems to the analyst. Unless the original sample is submitted in the form of a solution, it is necessary in most cases to dissolve it. Frequently, U or Pu must be separated from interfering elements prior to chemical analysis. Generic problems, sampling, dissolution, and separations are discussed in this chapter ahead of those sections on specific analytical techniques. Analytical techniques for U and Pu are discussed separately, except in two instances when the two elements are determined simultaneously: isotope dilution mass spectrometry and X-ray fluorescence spectrometry.

References 1 through 17 at the end of this chapter list publications on the chemical determination of U and Pu useful for general reference.

4.2 GENERIC PROBLEMS

The process of radioactive decay must be taken into account when developing procedures for the analysis of Pu- or U-bearing material. The high radiation fields in solutions containing Pu, fission products, ^{233}U, or other actinides can cause sample heating, solvent decomposition, reagent

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degradation, and oxidation/reduction reactions. For instance, in product solutions of reactor-grade Pu, there will be high alpha-radiation levels, and dissolver solutions in a reprocessing plant will have intense beta/gamma radiation because of the high concentration of fission products.

4.2.1 Heat

The major effect of heat generation is a change in the concentration of the solution as a result of evaporation. In the Pu product storage tanks of a reprocessing plant, evaporation could result in apparent concentration changes of several tenths of a percent per week if fresh acid were not added continually to the system. Even in closed containers, such as those used in the storage of archival samples and standards, significant volume changes can occur (Ref. 18).

4.2.2 Radiation

Alpha radiolysis causes decomposition of solvents, such as water and acids. The major reactions for water decomposition are as follows:

$$H_2O \longrightarrow H^\bullet + OH^\circ \qquad (4\text{-}1)$$

$$OH^\bullet + OH^\bullet \longrightarrow H_2O_2 \qquad (4\text{-}2)$$

$$H^\bullet + H^\bullet \longrightarrow H_2 \qquad (4\text{-}3)$$

with an overall production of hydrogen peroxide and hydrogen (Ref. 19). Some oxygen is also produced through the reactions

$$H^\bullet + O_2 \longrightarrow HO_2^\bullet \qquad (4\text{-}4)$$

$$HO_2^\bullet + HO_2^\bullet \longrightarrow H_2O_2 + O_2 \qquad (4\text{-}5)$$

The rate of the radiolytic decomposition of water is decreased by increasing the acid concentration.

Many analytical schemes call for the Pu to be either in nitric acid or sulfuric acid solution. For nitric acid, the decomposition reactions are

$$NO_3^- + H^\bullet \longrightarrow NO_2 + OH^- \qquad (4\text{-}6)$$

$$2NO_2 + H_2O \longrightarrow H^+ + NO_3^- + HNO_2 \qquad (4\text{-}7)$$

$$H^+ + OH^- \longrightarrow H_2O \qquad (4\text{-}8)$$

This competition for the hydrogen radical results in an overall decrease in formation of H_2 relative to that observed in water.

Radiolytic decomposition of sulfuric acid yields H_2O_2 as the most important product. In addition, H_2, $H_2S_2O_8$, and H_2SO_5 are formed. The main mechanism for the formation of hydrogen peroxide is the combination of two hydroxyl radicals. It has been stated (Refs. 20 and 21) that sulfuric acid scavenges OH radicals in the bulk of the solution. As the sulfuric acid concentration increases beyond certain limits (which will most likely be exceeded in Pu solutions for analysis), the H_2O_2 yield decreases, owing to inhibition of the reaction of the OH radical with molecular hydrogen or with itself, and the decomposition of H_2O_2 by the resulting sulfate ions. The reactions are postulated to be (Ref. 20)

$$H_2SO_4 + OH^{\circ} \longrightarrow SO_4^{-} + H^{+} + H_2O \qquad (4\text{–}9)$$

$$SO_4^{-} + H_2O_2 \longrightarrow SO_4^{2-} + H^{+} + HO_2^{\bullet} \qquad (4\text{–}10)$$

These reactions have a significant effect on the solution chemistry of Pu. The decrease in solvent content leads to a gradual increase in Pu concentration. The hydrogen peroxide formed will reduce any Pu(VI) to Pu(IV) and will oxidize Pu(III) to Pu(IV) with a resultant formation of O_2. This causes a pressure buildup in the sample container and could lead to explosions in closed systems containing significant amounts of Pu(VI). It has been shown that Pu in 8*M* HNO_3 is reduced almost quantitatively to Pu(IV) over a 2-week storage period (Ref. 22).

Most analytical methods for determining plutonium have been developed using weapons-grade Pu, which is predominantly ^{239}Pu. When these methods are applied to reactor-grade Pu, which contains significant concentrations of ^{238}Pu (an intense alpha emitter) and ^{241}Pu (an intense beta emitter), some problems may be encountered. Irradiation may decompose organic reagents used for extraction of Pu and may decrease the efficiency of extraction (Ref. 23). Plutonium oxalate is susceptible to decomposition by alpha radiation (Ref. 24, p. 407). Scientists working with ^{238}Pu have pointed out the need for special techniques (Ref. 25). Because a higher probability exists for radiation-induced reduction of Pu(VI) to Pu(IV) and oxidation of Pu(III) to Pu(IV), greater care must be exercised to minimize these reactions during analysis. Precision and accuracy for analysis of reactor-grade material may well be poorer than literature values obtained for weapons-grade material.

Material containing Pu or macro amounts of ^{233}U should be handled in glove boxes. Irradiated material is handled in shielded hot cells.

4.2.3 Polymerization

A green colloidal polymer of Pu(IV) can form by hydrolysis in Pu solutions in which the acid concentration is not sufficiently high. The rate of polymer formation (Ref. 26) is a function of Pu concentration, acid concentration, and temperature. In general, it has been found that the lower the ratio of the acidity to the Pu concentration, the greater is the rate and extent of polymerization (Ref. 27, p. 84; Ref. 28).

The presence of polymer is undesirable both in process operations and in analysis. In the plant, polymer formation can result in the precipitation of Pu in storage tanks and the adsorption of Pu on the walls of the process-stream pipes and tanks, where it may represent a criticality hazard. The presence of polymer means that a representative sample cannot be obtained. The polymer interferes with ion-exchange separations and either does not extract into many common solvents or causes emulsification. Polymeric Pu is not included in the results of some analytical techniques, such as coulometry.

Plutonium nitrate should never be stored at acid concentrations below 0.5*N*; a range between 2 and 10*N* is recommended. Even a localized, instantaneous decrease in acid concentration can cause polymer formation. For this reason, Pu solutions should never be diluted with water but rather with acid.

A spectrophotometric method for checking the presence of colloidal polymer in a plutonium nitrate solution is to extract the monomeric $Pu(NO_3)_4$ into tributylphosphate. The polymer does not extract; it can be identified by its absorption spectrum (Refs. 29 and 30).

Once the polymer has formed, it is difficult to decompose. Decomposition can be hastened by an increase in temperature, an increase in acid concentration, oxidation to Pu(VI), or reduction to Pu(III). The simplest treatment appears to be to adjust the nitric acid concentration to 5*N* and to boil the solution for an hour or two. In analytical schemes, fuming with concentrated perchloric acid and a few drops of hydrofluoric acid is often done to destroy polymer. Precautions to be observed when using perchloric acid fuming are described in Reference 31, p. 3–5.

4.2.4 Radioactive Decay and Isotopic Composition

The isotopic composition of U and Pu must be taken into account when making precise chemical measurements. The atomic weight of natural U (containing 0.7196 atom percent ^{235}U) is 238.032. For other U enrichments, the appropriate atomic weight must be calculated for many analytical techniques. When the isotopic abundance is given in atom percent, the atomic weight is simply the sum of the products of the nuclidic masses and the atomic fractions of the isotopes. When the isotopic abundance is given in weight percent,

$$\text{at. wt.} = \frac{100}{\dfrac{\text{wt. \% isotope A}}{\text{nuclidic mass isotope A}} + \dfrac{\text{wt. \% isotope B}}{\text{nuclidic mass isotope B}} + \ldots}$$

The nuclidic masses of uranium are as follows:

Nuclide	Nuclidic Mass
^{232}U	232.0372
^{233}U	233.0395
^{234}U	234.0409
^{235}U	235.0439
^{236}U	236.0457
^{238}U	238.0508

The isotopic composition of a Pu sample depends on the mode of production and the history of the sample. For material generated by the irradiation of light-water reactor (LWR) fuel, the isotopic composition is dependent on the original U enrichment, original Pu concentration and composition, fuel burnup, and period of cooling. The atomic weights for various Pu samples may differ significantly, and appropriate isotopic correction factors must be applied to analytical values. The atomic weight is calculated in the same way as described for U. Table 4.1 gives a listing of the Pu nuclides, their half-lives, and their nuclidic masses.

Table 4.1 Nuclidic masses and half-lives of plutonium isotopes

Nuclide	Half-Life[a] (yr)	Nuclidic Mass
^{238}Pu	87.74	238.0495
^{239}Pu	24,119	239.0522
^{240}Pu	6,537	240.0538
^{241}Pu	14.40	241.0569
^{242}Pu	3.87×10^5	242.0588

[a] Refs. 32 and 33.

An important consequence of radioactive decay is the change in isotopic abundance values and in Pu content with time. In the case of National Bureau of Standards (NBS) reference materials, for instance, it is common practice in analytical laboratories to correct the isotopic abundance values certified by NBS for the beta decay of ^{241}Pu to ^{241}Am. Marsh et al. (Ref. 34) have pointed out that the effects of the radioactive decay of ^{238}Pu, ^{239}Pu, ^{240}Pu, and ^{242}Pu to their U daughters can exceed that of ^{241}Pu decay, depending on the Pu isotopic distribution of the material. This is especially true for materials like the NBS Standard Reference Materials certified for Pu assay use, which have low ^{241}Pu isotopic abundance. Reference 34 contains detailed calculations for correcting isotopic abundance values and obtaining the Pu mass decrease, the U mass increase, the Pu content of the sample, and the Pu atomic weight, all as a function of time.

The growth of ^{241}Am in a Pu sample can interfere during subsequent determinations of Pu. For instance, Am may interfere (Ref. 35) with the amperometric determination of Pu. Americium must be removed prior to mass spectrometry or alpha spectrometry of Pu.

4.3 INHOMOGENEITY AND SAMPLING

4.3.1 Introduction

Analytical results are misleading and useless when the composition of the samples analyzed is not representative of the bulk material from which the sample was withdrawn. Representativeness can usually be achieved by sampling methods and/or plans that provide an equal chance for every portion of the material that varies in composition to be included in the sample. Analytical results based on representative samples will provide the best attainable unbiased estimate of the true U or Pu concentration of the bulk material with minimum error due to sampling.

The representativeness of the sample depends on both the homogeneity of the material being sampled and the sampling method or plan. Obviously, samples of homogeneous materials tend to be representative regardless of the sampling method or plan chosen. On the other hand, representative sampling may be difficult to achieve on grossly inhomogeneous materials, even with the most advanced random sampling methods or plans.

There are three types of inhomogeneity of SNM-bearing materials: (1) inhomogeneity in bulk material within a container; (2) inhomogeneity among containers of material (can to can, tank to tank); and (3) inhomogeneity among groups of containers (batch to batch, lot to lot, category to category).

This section briefly describes general methods for mixing inhomogeneous bulk materials, grouping containers into homogeneous lots, and random sampling of bulk materials. The performance of mixing and sampling methods on common materials processed in nuclear fuel production facilities is presented in Tables 4.2 and 4.3 to guide method selection.

4.3.2 Mixing Materials That Exhibit Within-Container Inhomogeneities

Each container to be sampled should be thoroughly mixed or blended before sampling, using techniques that result in maximum homogeneity. Simple liquids or solutions that do not contain suspended solids (or other phases) can be mixed by stirring, sparging, or recirculation pumping. When the solution contains suspended solids or other phases, mixing is difficult by any method. The solids should be separated from the solution or dissolved before mixing and sampling whenever possible. If a multiphased liquid must be sampled, sampling should be performed by the most effective random method during the mixing operation.

Table 4.2 Elemental inhomogeneity of uranium-bearing materials

Application	Mixing and Sampling Methods	Type of Inhomogeneity	Random Sampling Error (% RSD)
UO_2 powder:			
87.6% U in 5-gal. metal cans (20 kg)	Mix (tumble end to end) 12 min. core sample one 50-g sample from each of 3 cans per lot, 1 sample per can.	Can to can	0.032[a]
88% U in 3-gal. shipping containers (25 kg)	Grab sample (scoopula) one 5-g sample per container, 1 container per batch.	Batch to batch	0.005[a]
88% U in 12-in diameter by 18-in. high polylined can (29 kg)	Grab sample (scoop) 10 g from 3 in. below top center, each of 3 randomly selected cans per lot.	Can to can	0.014[a]
87% blend in 12-in. high by 10-in. diameter fiberpacks (18 kg)	Mix (roll) 10 min, core sample three 30- to 40-g samples and composite.	Pack to pack	<0.020[a]
Blend material in cans	Mix (V-cone blend) 10 min 2 cans of a several-can-blend batch, grab sample (scoop) two 50-g samples from each blended can.	Within can	<0.027[a]
UO_2 pellets:			
88% U in 100 tray lots, 900 to 1200 pellets per tray	Random selection of 1 pellet every 25 trays (4 pellets), composite, crush.	Lot to lot	<0.020[a]
88.1% U in pellet trays	Random selection of 5 pellets from last third of pellet lot.	Within lot	<0.025[a]
88% U in 290-boat (2000 pellets per boat) lot	Random selection of 5 pellets from each third of lot, composite and chunk each 5-pellet third.	Within lot	<0.008[a]
U_3O_8 powder, 75% subblend in 12-in. high by 10-in. diameter fiberpacks (18 kg)	Mix (roll) 10 min, core sample three 30- to 40-g samples and composite.	Pack to pack	2.2[a]

Note—See footnote at end of table.

Table 4.2 Elemental inhomogeneity of uranium-bearing materials (Cont'd)

Application	Mixing and Sampling Methods	Type of Inhomogeneity	Random Sampling Error (% RSD)
UO_2, U_3O_8 powder, HTGR feed in 1-gal. can (3.5 kg)	Core sample 15-g sample from each can, composite, duplicate analyses.	Lot to lot	0.01
Uranium metal, sheets, TRIGA feed	Random selection of duplicate samples from 20% of the sheets per lot.	—	$<0.06^b$
(U,Th) oxide powder, HTGR material in ½- to 1-gal. polyethylene bottles (≈1 kg)	Core sample duplicate 15-g samples.	—	0.04 to 0.18^b
(U,Th) oxide, SiC coated, HTGR material in ½- to 1-gal. polyethylene bottles (≈1 kg)	Core sample duplicate 15-g samples.	—	0.4^b
(U,Th) carbide particles, 100- to 300-μm size in 8- to 9-kg metal bottles	Split (10-way splitter) duplicate 15-g samples from each of 2 bottles every 10 bottles.	—	0.03 (300 μm)^b 0.19 (100 μm)^b
(U,Th) carbide, SiC coated, 100- to 400-μm particles in 1-gal. metal cans (3.6 kg)	Mix, Hobeg proportional rotary stream splitter (1/10), collecting 30 g, split (riffle) to duplicate 15 g samples.	—	0.40 (100 μm)^b 1.3 (300 μm)^b
U-Zr alloy, hydride:			
Powder (TRIGA fines) in ½- to 1-gal. polyethylene bottles (1 kg)	Core sample three 5-g samples and composite.	—	2.4^b
Short rods (TRIGA meats), 0.5- to 1.5-in. diameter by 5- to 5.5-in. long	Random selection of 2 rods (large meats) or 3 rods (small meats), machine 1 to 2 g from each end of each rod.	—	0.65^b
Uranyl nitrate solutions in cylindrical 300-gal tank with Raschig rings	Mix (circulate), petcock sample (tap in circulate line) 10- to 20-mL sample, remix, withdraw second sample.	Within tank	0.22^a

Note—See footnote at end of table.

Table 4.2 Elemental inhomogeneity of uranium-bearing materials (Cont'd)

Application	Mixing and Sampling Methods	Type of Inhomogeneity	Random Sampling Error (% RSD)
HEU dissolver solutions in critical safe tanks, 5-in. diameter by 6-ft high	Mix (circulate between tanks) 20 min, withdraw (spigot at pump outlet) 10-mL sample, remix 5 min, withdraw second sample.	Within tank	0.86[a]
Clean scrap: homogeneous UO_2 powder with $(NH_4)_2C_2O_4$ and NH_4HCO_3	Mix (mechanical blend), grab sample duplicate samples, duplicate analyses per sample.	Within container	0.03
Dirty scrap:			
UO_2/U_3O_8 powder in 5-gal. metal cans (20 to 35 kg)	Mix (tumble) 12 min, grab sample (scoopula) replicate 40- to 50-g samples from top center, replicate analyses per sample.	Within can	3.7
Inhomogeneous UO_2 powder, Gd_2O_3, NH_4HCO_3, $(NH_4)_2C_2O_4$, hard scrap	Grab sample duplicate samples, duplicate analyses per sample.	Within container	0.6
Sludge, sweepings, ash, filter knockdown (30% to 79% U) in 2- to 3-gal polyethylene-lined fiberpacks (15 kg)	Core sample four 50-g samples per container; sample only certain proportion of the containers in a special material category.	Within container	6.4 (0.8 to 23)
Calcined material (30% U) in calciner boats	Grab sample (scoop) two 10-g samples from surface.	Within batch	9.1[a]
Incinerator ash (30% U) in 2-L polyethylene bottle	Mix (ball mill) 30 min, grab sample two 10-g samples from ball mill dump stream (into bottle).	Within bottle	24[a]
Ash ($\approx$31% U) 18-in. high by 10-in. diameter cans (12 kg)	Grab sample (scoop) 50-g sample from top quarter of can.	Can to can	13[a]

Note—See footnote at end of table.

Table 4.2 Elemental inhomogeneity of uranium-bearing materials (Cont'd)

Application	Mixing and Sampling Methods	Type of Inhomogeneity	Random Sampling Error (% RSD)
Grinder sludge in 5-gal. plastic bucket (18 kg)	Mix (stir with scoopula), grab sample (scoopula) replicate 20- to 25-mL samples top center, replicate analyses per sample.	Within can	3.5
ADU (wet, clay-type) in 5-gal plastic bucket (18 kg)	Mix (stir with scoopula), grab sample (scoopula) replicate 20- to 25-mL samples top center, replicate analyses per sample.	Within can	12
(U-Zr) oxide, very fine powder (TRIGA solids and sludges) in 2-L polyethylene bottles	Mix (roll mill) 15 min, core sample duplicate 5-g samples.	—	2.4[b]
Raffinate solution in 300-gal. cylindrical tank with Raschig rings	Mix (circulate), petcock sample (tap in circulation line) 10- to 20-mL sample, remix, withdraw second sample.	Within tank	0.62[a]

[a] Estimated (see text).

[b] Method for calculating error is not defined.

Table 4.3 Isotopic inhomogeneity of uranium-bearing materials

Application	Mixing and Sampling Methods	Type of Inhomogeneity	Random Sampling Error (% RSD)
UO_2 powder, blend material (LEU) in 12-in. high by 10-in. diameter fiberpacks (18 kg)	Mix (stratify), grab sample (1-g spoon) one 1-g sample from each of 4 fiberpacks (different levels).	Pack to pack	0.24[a]
UO_2 pellets, (LEU) material in 100-tray lots, 900 to 1200 pellets per tray	Random selection of one pellet every 25 trays, composite, crush.	Lot to lot	0.39[a]
UO_2 powder and pellets, pure and scrap (LEU) in multilot projects of varying enrichments	Grab sample, 1 sample per lot for pure powder, 2 samples per lot for pellets, 3 samples per lot for scrap powder.	Lot to lot	0.31
Ash (LEU) in 18-in. high by 10-in. diameter can (12 kg)	Grab sample (scoop) one 50-g sample from top half of each can.	Can to can	1.9[a]

[a] Estimated (see text)

Some particulate and powdered materials such as incinerator ash and calcined scrap may also be difficult to mix. Factors that affect homogenization of dry powders or particulate material (in order of importance) are the following (Ref. 36):

(1) Composition variation as a function of factors such as particle size, density, and shape
(2) Range of particle size
(3) Range of particle density
(4) Range of particle shapes
(5) Interparticle cohesion or adhesion.

The process by which particles are mixed has been examined by a number of investigators. The mixing classifications were listed by Lacey (Ref. 37). He defines three mixing motions:

(1) *Diffusive mixing*—a process that occurs when particles roll over a sloping surface of the remainder of a pile of particles; for example, rolling and pouring.
(2) *Shear mixing*—a process that occurs when slip planes are established within the powder; for example, stirring.
(3) *Convective mixing*—a process that occurs when circulation patterns are set up inside the powder mass; for example, strong vibration.

When the particles are relatively uniform, all three of these actions will lead to a random mix. However, if the particles have a wide range of physical properties (that is, size, shape, and density), the diffusive and shear motions tend to resist mixing or to segregate the particles. These two methods involve the movement of a small fraction of the material in close proximity to a relatively motionless mass of particles, which promotes segregation. Since convection motion involves the movement of a relatively large fraction of the mass of particles, there is much less tendency to segregate, and mixing is, therefore, more likely to occur (Ref. 38). Table 4.4 presents a qualitative evaluation of available blenders that may be used to mix particles that exhibit a great tendency to segregate.

4.3.3 Homogenizing Materials That Exhibit Inhomogeneities Among Containers or Groups of Containers

When a group of containers exhibits very small can-to-can inhomogeneities, containers to be sampled and analyzed can be selected randomly from the group. Each can is, therefore, afforded an equal chance of being selected. If, however, the can-to-can inhomogeneities are large, then large sampling errors can result from the random selection method. It is therefore important to segregate the cans into homogeneous groups before using the random selection method. The grouping into homogeneous

Table 4.4 Summary of mixer characteristics

Type of Mixer	Batch or Continuous	Main Mixing Mechanism	Segregation (Suitability for Ingredients of Different Properties)	Axial Mixing	Ease of Emptying	Tendency to Segregate on Emptying	Ease of Cleaning
Horizontal drum	Batch	Diffusive	Bad	Bad	Bad	Bad	Good
Lödige mixer	Batch	Convective	Good	Good	Good	Good	Bad
Slightly inclined drum	Continuous	Diffusive	Fair	Bad	Good	Good	Good
Steeply inclined drum	Batch	Diffusive	Bad	Good	Bad	Bad	Good
Stirred vertical cylinder	Batch	Shear	Bad	Good	Good	Bad	Good
V mixer	Batch	Diffusive	Bad	Bad	Good	Bad	Good
Y mixer	Batch	Diffusive	Bad	Bad	Good	Bad	Good
Double cone	Batch	Diffusive	Bad	Bad	Good	Bad	Good
Cube	Batch	Diffusive	Poor	Good	Good	Bad	Good
Ribbon blender	Batch	Convective	Good	Slow	Good	Fair	Fair
Ribbon blender	Continuous	Convective	Good	Fair	Good	Good	Fair
Air-jet mixer	Batch	Convective	Fair	Good	Good	Good	Fair
Nauta mixer	Batch	Convective	Good	Good	Good	Good	Bad

categories (strata), followed by random selection of cans to be sampled and analyzed within each category, is called the random stratified selection method and tends to reduce sampling errors resulting from can-to-can inhomogeneities. The use of the random stratified selection method is especially important for taking inventory at the beginning and end of safeguards reporting periods.

Stratification of containers into homogeneous groups is usually not a problem for feed and product materials that are uniform, well characterized, and identified with batches or lots of production material. Scrap and waste materials, however, have a wide range of physical properties and chemical compositions. These materials are usually not well characterized, and the SNM concentration may vary widely from can to can. Accordingly, it is usually necessary to presort scrap materials prior to packaging to avoid large can-to-can concentration variations. Careful stratification of the cans into homogeneous groups according to SNM concentration prior to random selection of containers to be sampled will further reduce sampling error.

4.3.4 Common Random Sampling Methods (Ref. 39)

Techniques for taking sample increments vary from simple dip or grab sampling to the use of sophisticated mechanical devices which select a fraction of the entire cross section of material in a container or flowing stream. The choice of sampling method depends on the homogeneity of the material relative to the required measurement precision, the kind and number of items or containers to be sampled, accessibility, and safety hazards involved. Materials encountered in the nuclear industry frequently are not sufficiently homogeneous to permit reliance on arbitrary sampling methods such as grab sampling from easily accessible parts of the materials. Therefore, random sampling or the closest practical approach to random sampling should be used. This requires sample increments to be selected in such a way that every possible increment in the population has a finite and predictable chance of selection.

Techniques and devices in common use for sampling liquids and powders and adaptable to random sampling are:

(1) *Liquid thief probe*—a closed bottle or tube that can be opened for filling at any desired level in the liquid.

(2) *Powder thief probe*—a closed tube that is inserted into a material and then opened to allow filling at the desired place in the powder (usually along the full length of the probe).

(3) *Vacuum or pneumatic probe*—an open-ended tube that can be evacuated to draw a powder or liquid through the tube and into a sample receiver. The tube is inserted into the material at the same rate the material flows up the tube.

(4) *Core sampler*—an open-ended tube for insertion into material that is sufficiently viscous or cohesive to remain in the tube when the tube is withdrawn.

(5) *Dip tube*—similar to a core sampler; that is, a simple, open-ended, small-diameter tube inserted slowly into a liquid, then closed at the top to prevent outflow when the tube is withdrawn.

(6) *Auger sampling probe*—sheathed auger that draws the material up the tube when it is being inserted (analogous to a vacuum probe).

(7) *Flowing-stream sampler*—a stream splitter that withdraws a portion of the moving material either continuously or periodically. This type of sampler is readily automated, and many variations on this design are used in powder and liquid sampling [see (10) spinning disk sampler].

(8) *Outlet sampling*—manual or mechanical withdrawal of a portion from a conveyor or mixer outlet. In the case of liquids the withdrawal may be from the drain line.

(9) *Petcock sampling*—withdrawal of liquid sample from a flowing stream, a tank, or a recirculating line on a tank through a fixed tube and valve.

(10) *Spinning disk sampler*—a rotating device that captures a small increment (a complete cross-sectional portion) of a flowing stream at frequent intervals during the time the material is flowing.

(11) *Sample splitter*—a splitter is a device that randomly withdraws a sample of material from that introduced to the splitter.

4.3.5 Sampling Performance

From the preceding discussion in this section, it is clear that the performance of sampling methods depends on a number of parameters not related to the sampling method itself including

(1) Physical and chemical characteristics of the material sampled
(2) The amount and type of inhomogeneity within the material
(3) The mixing method and other preconditioning methods used prior to sampling
(4) The size, shape, and other characteristics of the containers to be sampled.

During the users' survey of nuclear fuel production facilities, the performance of various methods used under specific circumstances was quoted or calculated from available data. These performance data observed for common material types, mixing methods, sampling methods, and other conditions are listed in Tables 4.2 and 4.3.

The sampling errors reported in the tables fall into two categories depending on how they were estimated. Performance values not footnoted indicate that the facilities determined random sampling error by taking replicate samples and performed replicate analyses on each sample. The sampling error can then be separated from the analytical error:

$$\sigma_s = (\sigma_t^2 - \sigma_a^2)^{1/2} \tag{4-11}$$

where

σ_s = random error due to sampling

σ_t^2 = pooled random variance of all analyses on all samples

σ_a^2 = random variance estimated from the replicate analyses performed on each sample

At some facilities, however, replicate analyses were not performed on each sample, and the random sampling error was not reported separately from random analytical error. In these cases, the random sampling error was roughly estimated by assuming that variance based on replicate analyses of standards is approximately equal to the random analytical variances and that

$$\sigma_s = (\sigma_s^2 - \sigma_{st}^2)^{1/2} \tag{4-12}$$

where

σ_s = estimated random sampling error

σ_s^2 = random variance based on a single analysis of replicate samples

σ_{st}^2 = random variance based on replicate standard analyses

Because differences between the samples and the standards other than inhomogeneities may affect the random analytical variance, these values are considered rough estimates of sampling error. When a "less than" value is reported, the sampling error appeared to be less than the analytical error.

Two general conclusions can be drawn from these data: (1) feed and product U-bearing materials tend to be homogeneous and, therefore, only relatively simple sampling methods are required to obtain fairly representative samples; and (2) scrap and waste materials are especially inhomogeneous, and sampling errors are significant. To avoid large sampling errors, an appropriate mixing method should be selected to homogenize the material to be sampled as much as possible and a suitable random sampling method should be used to withdraw a representative sample. A more detailed discussion of sampling considerations and calculations of sampling errors are presented in the literature cited in References 39 through 43.

4.4 SAMPLE DISSOLUTION

4.4.1 Introduction

In many analytical procedures the step that follows sampling is dissolution of the sample. The dissolution must be complete and quantitative, and the resulting solution must be amenable to the chosen method of analysis. Thus, the chemicals and techniques used in dissolution will depend on the particular requirements of the analytical method (Refs. 41, 42, and 43). For these requirements, the discussions of individual procedures in this handbook or in the original papers should be consulted. In this section, a general discussion of dissolution techniques is presented.

Dissolution of U and its compounds is relatively straightforward. However, the silicon-carbide-coated $(U,Th)C_2$ kernel fuel used in several types of high-temperature reactors presents a unique dissolution problem (Ref. 44). In the case of Pu and its compounds, the dioxide presents special problems due to its refractory nature. The higher the firing temperature, the more refractory the material becomes and the more resistant it is to dissolution. Plutonium oxide that has been fired below 800°C is fairly readily dissolved by means of appropriate acids. Oxide that has been fired at temperatures greater than 800°C is more difficult to dissolve. Fusion techniques or a combination of acid dissolution and fusion techniques may be required (Ref. 45).

Mixed plutonium-uranium oxide retains most of the refractory nature of plutonium dioxide, but its dissolution rate is more rapid than that of plutonium dioxide alone (Ref. 46). Mixed oxide usually can be dissolved in acids, but sometimes fusion techniques are required. It may be necessary to use both treatment with acid and fusion to effect a complete dissolution of some samples (Ref. 44).

In the following sections, various dissolution techniques will be briefly discussed. For detailed procedures, the reader is referred to the references cited.

4.4.2 Uranium-Bearing Materials (Refs. 42, 44, 47, and 48)

4.4.2.1 Nitric Acid Dissolution

Uranium metal and many of its compounds are readily soluble in concentrated nitric acid (15.9 M; sp gr, 1.42). This acid is generally used when nitrate ion can be tolerated in the analytical method to be used.

Dissolution of pellets can be hastened by breaking them into smaller pieces by means of a Plattner mortar, using a hammer to impart a single sharp blow on the pestle. The pieces should not be subsequently ground to a powder because impurities may be introduced into the sample and excessive oxidation of the uranium dioxide can occur. (Oxidation will preclude weighing a sample that represents the original stoichiometry of the pellet.)

4.4.2.2 Phosphoric Acid Dissolution

Phosphoric acid (14.8 *M*; sp gr, 1.70), along with hydrofluoric acid, is used to dissolve large amounts (3 g or more) of sample when the high-precision version of the Davies and Gray/New Brunswick Laboratory (NBL) method is used. Phosphoric acid is used here to provide a non-oxidizing dissolution medium so that an excessive amount of reductant, Fe(II), will not be necessary. Dissolution of uranium dioxide powders with the acid mixture is satisfactory but may be quite slow for pellets. Dissolution of whole pellets in phosphoric acid is not practical because of the slow dissolution rate. Broken pellets weighing about 0.25 g can be dissolved in less than 3 h under reflux conditions.

4.4.2.3 Perchloric Acid Dissolution

Perchloric acid (11.7 *M*; sp gr, 1.67) is recommended for the dissolution of 5-g uranium dioxide samples when using the Jones reductor/dichromate titration method. Nitric acid is avoided here because of nitrate interference in the analytical procedure. The dissolution must be performed in a manner that prevents spray loss of U during fuming. A suitable apparatus is shown on page 3–3 of Reference 42.

4.4.2.4 Sulfuric Acid Dissolution

It is sometimes necessary to fume solutions of large samples (3 to 5 g) to expel volatile interfering substances. The apparatus recommended for the perchloric acid dissolution is also recommended for fuming with sulfuric acid.

4.4.2.5 Dissolution of Uranium-Bearing Material (Ref. 47)

Procedures used at NBL for dissolution of a variety of U-bearing materials are as follows:

Material	Treatment
U, UO_3, U_3O_8, UF_4	Dissolve in HNO_3. Fume sample aliquots with H_2SO_4.
UO_2 powders and pellets, ammonium diuranate, wastes, and UO_2-ThO_2	Dissolve in HNO_3, filter, fuse residue in $NaHSO_4$ or Na_2CO_3, combine solutions. Fume sample aliquots with H_2SO

Material	Treatment
Ore concentrates	Dissolve in HNO_3, fume sample aliquots with H_2SO_4 and HF.
HTGR fuel beads (SiC-coated, pyrolytic carbon-coated, U-Th carbide)	(1) Ignite to remove carbon, fuse with Na_2CO_3, dissolve cake and fume with H_2SO_4 and HF to remove silica. Precipitate U with NH_4OH to remove excess fusion salts, dissolve residue in HNO_3. Fume sample aliquots with H_2SO_4. (2) Ignite to remove carbon, treat with Cl_2 at 900°C to decompose SiC, ignite as in (1), dissolve as with UO_2-ThO_2.
UC and UC_2	Ignite, dissolve in HNO_3, fuse any residue. Fume sample aliquots with H_2SO_4.
U-Al, U-Si, and UO_2-SS	Dissolve in HCl-HNO_3, fume with $HClO_4$, filter. Volatilize silica with HF, fuse remaining residue with Na_2CO_3. Fume sample aliquots with $HClO_4$.
Fissium alloy, and fissium dross	Dissolve in HCl-HNO_3; treat residue with NaOCl and NaOH, acidify with HCl, combine solutions. Fume sample aliquots with $HClO_4$. (Residue from dross requires fusion with NaOH).
Ash samples	Fuse with Na_2CO_3-$NaNO_3$ (5:1) and/or $NaHSO_4$, dissolve cake in HNO_3-$HClO_4$, volatilize silica with HF, fume with $HClO_4$. Fume sample aliquots with H_2SO_4.
UO_2-ZrO_2-Nb-Zr and UO_2-BeO	Dissolve in HNO_3-HF. Fume sample aliquots with H_2SO_4 or $HClO_4$. (Large quantities of Nb may be removed by precipitation with SO_2.)
Dissolver solutions, organic solutions, and wastes	Homogenize and reconstitute multiphase mixtures where necessary. Destroy organics with hot H_2SO_4-HNO_3. Fume sample aliquots with H_2SO_4.
U-Zr	Dissolve in HF. Fume sample aliquots with H_2SO_4 or $HClO_4$.

4.4.3 Plutonium-Bearing Materials (Ref. 41)

4.4.3.1 Acid Dissolution

Using only acids, plutonium metal and refractory plutonium dioxide may be dissolved in 12 to 16*M* HNO_3 containing 0.05 to 0.25*M* HF (Refs.

46, 48, and 49). Oxide fired below 800°C is dissolved readily in hot 8*M* HNO_3–0.1*M* HF, the acid mixture most commonly used for this material (Ref. 45). Often the addition of one or two drops of 48% HF late in the dissolution will hasten the dissolution, especially when high-fired material is being treated.

It has been reported (Ref. 49) that plutonium dioxide fired at temperatures below 950°C may be dissolved in 11*M* HCl–0.1*M* HF. The dissolution is carried out in Teflon beakers with close-fitting, but not sealed, lids at a temperature of 95°C to 100°C.

An acid-dissolution mixture that will allow a somewhat elevated dissolution temperature and that is suitable for high-fired plutonium dioxide and mixed plutonium-uranium or plutonium-thorium oxide fuels consists of 5 mL of 9*M* H_2SO_4, 1 mL of 14*M* HNO_3, and 2.5 g of ammonium sulfate (Ref. 50). Nitric acid is needed only if U is present. The sample is refluxed in the mixture for 30 min and then fumed for 2 h (4 h if plutonium-thorium oxide). After fuming, the cooled sample is diluted with water.

An acid-dissolution procedure using a sealed tube (Refs. 51 and 52) is useful in dissolving many refractory materials including high-fired plutonium dioxide (Refs. 53 through 56). This technique effects dissolution from the higher temperature (310°C to 325°C) and pressure (up to 2.8 MPa or 400 psi) produced within a silica tube. A fair amount of manipulation is required; however, dissolution at operating temperature can be obtained in 2 to 48 h, depending on the sample material. The acid mixture used in the tube is generally 7-mL of 12*M* HCl with several drops of 11.7*M* $HClO_4$, although good results have been reported with 15.9*M* HNO_3 in place of the $HClO_4$ (Ref. 56). Because of the high pressures involved, the technique should be used only by trained personnel and with appropriate supervision. The cited literature should be reviewed for a description of the apparatus and for the operating directions that must be rigidly followed.

Acid dissolution techniques using a sealed Teflon container surrounded by a metal shell have been reported (Refs. 57 and 58) for high-fired plutonium dioxide as well as a variety of other materials. This technique is essentially a variant of the sealed-tube technique; however, it is somewhat less hazardous. Dissolution times range up to 40 h at temperatures up to 275°C and pressures up to 34.5 MPa (5000 psi).

4.4.3.2 Fusions

In many cases fusion methods appear to be more satisfactory than acid treatment for the complete dissolution of refractory Pu materials (Ref. 59). Up to 1-g samples of refractory oxides can be readily dissolved by treating with sodium bisulfate at 600°C to 625°C for 20 to 25 min (Refs. 59 and 60).

Other fusion salts have been used for the dissolution of refractory oxides of Pu. A mixture of sodium hydroxide and sodium peroxide (Ref. 61) provides rapid dissolution, but attack of the fusion vessel can be a problem. Ammonium bisulfate (Ref. 62) has also been used; however, the time required for complete fusion is a minimum of 3 h. Mixtures of sodium bisulfate and potassium pyrosulfate (Ref. 63), sodium pyrosulfate and potassium pyrosulfate (Ref. 50), and potassium pyrosulfate and sodium peroxide (Ref. 64) have been recommended, but fusion with any of these mixtures may result in the formation of insoluble potassium salts of Pu (Ref. 65).

4.4.3.3 Combined Acid Dissolution and Fusion (Ref. 41)

When a sample cannot be completely dissolved by acid dissolution using HNO_3-HF and it is not practical to repeat the dissolution, the residue can be treated by fusion with sodium bisulfate. It is not necessary to filter off the residue and treat it separately; instead, both the solution and the residue can be transferred to a Pt dish, evaporated to dryness, and the resulting salts and residue fused with sodium bisulfate. This has been referred to as the leach-fusion technique (Ref. 66).

4.4.3.4 Other Considerations (Ref. 41)

An advantage of fusion with sodium bisulfate is that if ion-exchange purification of the sample solution is required, the use of hydrogen peroxide to convert the Pu to the tetravalent state is not needed since the fusion process apparently causes the desired conversion (Ref. 60).

The problem that can arise from fusion procedures as a result of impurities that may be present in the fusion salt must be recognized. Such impurities may be present in sufficient quantities to cause erroneous results. If, for example, Fe is present in both the fusion salt and the sample and interferes in the assay method, then the correction made for Fe must then be based on the concentration of Fe found in an aliquot of the same final solution used for the assay. Reagent-grade acids are usually very low in impurities and, as a result, acid dissolutions do not add interfering elements in significant quantities. Nevertheless, the analyst must recognize the possibility of introducing impurities when employing any dissolution procedure.

4.4.3.5 Dissolution of Plutonium-Bearing Materials (Ref. 47)

Dissolution procedures used at NBL for various plutonium-bearing materials are summarized as follows:

Materials	Treatment
Pu, Pu-Al, and Pu-Ga	$6N$ HCl or $18N$ H_2SO_4
U-Pu-Mo	$3N$ HCl–$8N$ HNO_3–$0.1N$ HF

Materials	Treatment
PuO_2 and PuO_2-UO_2	8*N* HNO_3–0.1*N* HF, or fuse in $NaHSO_4$
PuO_2 fired at temperatures in excess of 800°C	Fuse in $NaHSO_4$, or 8*N* HNO_3–0.1*N* HF (extended heating)
(U-Pu)C	Ignite, dissolve in 8*N* HNO_3–0.1*N* HF, or fuse in $NaHSO_4$
Calcined ash	Fuse in $NaHSO_4$ or leach in 8*N* HNO_3–0.1*N* HF and fuse residue in $NaHSO_4$
Brick residues: Al_2O_3, MgO, CaO, Fe_2O_3, and SiO_2	Fuse in $NaHSO_4$, dissolve in 2 to 8*N* HNO_3 and fuse residue in Na_2CO_3
Grinder sludge: SiC	Fuse in $NaHSO_4$

4.4.4 Mixed Fuel Materials (Ref. 43)

4.4.4.1 Acid Dissolutions

Using only acids, mixed plutonium-uranium oxide may be dissolved by heating the sample in a Teflon beaker with 15.9*M* HNO_3 containing 0.05 to 0.25*M* fluoride (Refs. 45 and 46). As with plutonium dioxide alone, the addition of a few drops of 48% HF late in the dissolution process will increase the dissolving rate, especially when pellets are being treated. Complete dissolution may take 4 to 8 h or more depending on the history of the sample.

The sealed-reflux dissolution system described in Reference 67 provides a rapid method for the dissolution of many refractory materials. In this simplified pressurized acid system, the sample and acid solution are heated in a specially designed glass reaction vessel (Figure 4.1) to 150°C at 0.57 MPa (82 psi). Under these conditions of relatively low temperature and pressure, up to 1 g of high-fired plutonium dioxide can be dissolved in 2 to 4 h. Dissolution of mixed oxides can be accomplished in 2 h or less at 150°C. An acid mixture of 5 mL of 12*M* HCl, 3 drops of 15.9*M* HNO_3 and 5 drops of 1.3*M* HF is recommended. Other acid mixtures can be used at higher temperatures and pressures as indicated in Reference 67. This procedure should be used with caution since the presence of large amounts of organic materials or metallic constituents can lead to the development of excessive pressures. An advantage of the sealed-reflux system is the automatic venting of pressures above approximately 1 MPa (145 psi) without loss of sample; this essentially eliminates the possibility of tube rupture because of high-pressure surges (Ref. 43). This system produces a solution relatively free from added contaminants, eliminates loss of sample from splattering, and is safe.

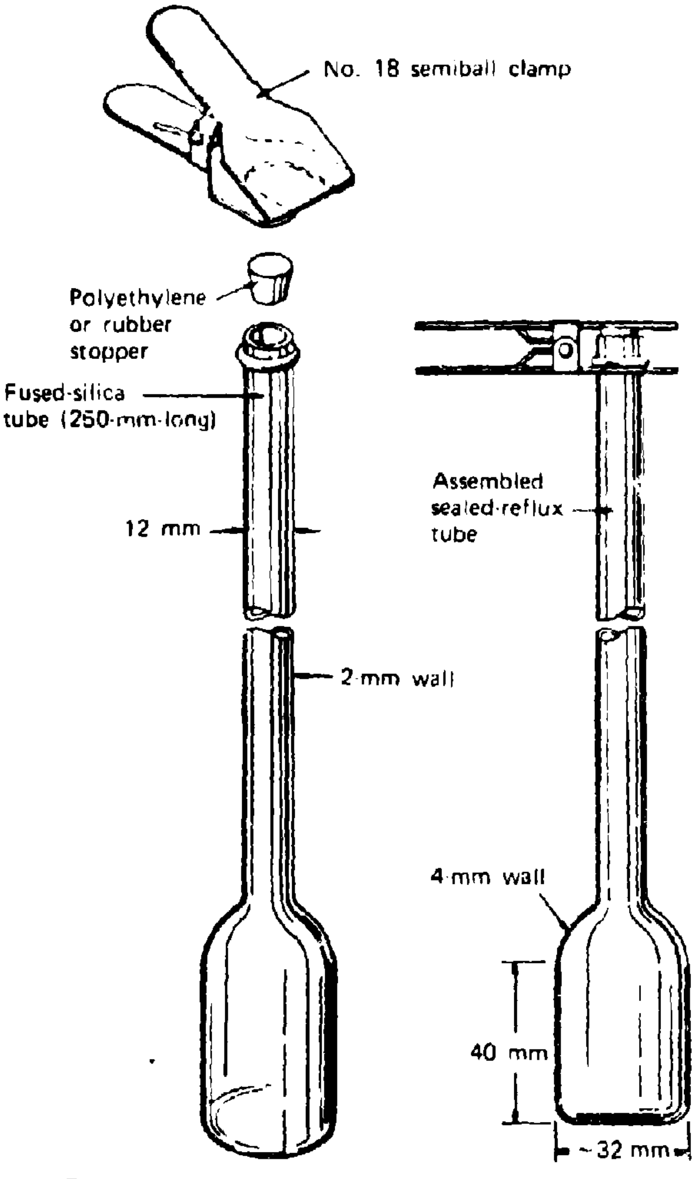

Figure 4.1 Sealed-reflux dissolution tube assembly (Ref. 67).

The Teflon-container metal shell technique (Refs. 57 and 58) mentioned in the section on Pu dissolution is also applicable to mixed-fuel materials and scrap materials. Various materials that have been successfully dissolved are listed in Table 4.5 Using this apparatus, whole mixed oxide pellets containing about 25% PuO_2, fired at 1600°C, were quantitatively dissolved with 15.9*M* HNO_3 in 12-h heating periods at 270°C. Mixed oxides could also be dissolved in concentrated HCl using this technique.

Uranium-thorium carbide fuel beads, coated with pyrolytic carbon and silicon carbide, have been dissolved using the Teflon container metal-shell technique (Ref. 57). Alternative dissolution procedures for this fuel have been described. Two of these (Refs. 44 and 47) are listed in Section 4.4.2.5 for HTGR fuel beads. A third procedure involves ignition in oxygen at 800°C to remove the outer carbon coating, volatilization of the SiC layer as $SiCl_4$ in a stream of chlorine gas at 1100°C to 1200°C, reignition in oxygen to remove the inner carbon coating, and dissolution of the uranium and thorium oxides remaining after the stripping process in a mixture of 8*M* $HNO_3$$-$0.05*M* HF (Refs. 68 and 69).

4.4.4.2 Fusions

It may be necessary to resort to fusion methods to obtain complete dissolutions of ceramic mixed fuel materials. The discussion of fusion methods and combined acid dissolution and fusion in Section 4.4.3 on Pu dissolution also applies to these materials.

Milner, Phillips, and Fudge (Ref. 70) discuss the dissolution of a variety of ceramic fuel materials. Their summary table of various procedures is included here as Table 4.6.

4.5 SEPARATION METHODS

After sampling and dissolution, the next step of an analytical procedure is often the separation of the actinides from each other or from other potentially interfering elements. For instance, solvent extraction of U precedes the fluorometric determination of that element in waste solutions, and an ion-exchange separation is always performed before the isotopic analysis of Pu by mass spectrometry, to separate Pu from U and Am.

Uranium commonly exists in solution in the hexavalent state as UO_2^{2+} and can be separated readily from Th, which exists in solution only in the tetravalent state. Plutonium is separated from uranium by adjusting the valence of Pu to Pu(III) or Pu(IV). Americium and the fission products are removed from U and Pu solutions by leaving them in the trivalent state, while U is present as U(VI) and Pu is present as Pu(IV) or Pu(VI).

Table 4.5 Dissolution of nuclear fuel cycle materials in teflon container metal-shell apparatus[a]

Material	Acid Mixture[b]	Shell	U or Pu Solubilized (%)[c]
$UO_2/ZrO_2/Nb$	HF/HNO_3	Ni	>99
	HNO_3/HF	Steel	>99
Nb/U alloy	HF/HNO_3	Ni	>99
	$H_2SO_4/HNO_3/HF$	Steel	>99
	H_2SO_4/HF	Steel	>99
U/Nb/Zr/Hf alloy	HF/HNO_3	Ni	>99
	HNO_3/HF	Steel	99
$UO_2/ZrO_2/Zr$	HCl	Ni	>99
PuO_2, high-fired	HNO_3/HF	Steel	>99
	$HCl/HClO_4$	Ni	>99
$(U, Pu)O_2$, 1600°C fired	HNO_3	Steel	>99
	HCl	Ni	>99
Scrap materials:			
U/calcined ash	HNO_3/HF	Steel	70 to 90
Dissolver sludge	HNO_3/HF	Steel	>99
	HCl/HF	Ni	>90
Brick fines	HNO_3/HF	Steel	<10
	HCl/HF	Ni	<10
UC/ThC/SiC/C/TRISO fuel[d]	HNO_3/HF	Steel	>99[e]
	$HNO_3/HF/H_2O_2$	Steel	>99[f]

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[a] From Ref. 57.

[b] Concentrated acids used with largest concentration acid listed first.

[c] Generally overnight reaction at 270°C to 275°C.

[d] HTGR fuel microspheres with UC/ThC kernel, pyrolytic carbon, and SiC coats.

[e] 0.1-g samples in 16*M* HNO_3/2*M* HF.

[f] 0.3-g samples in 0.5-mL 16*M* HNO_3/0.5-mL 29*M* HF, 5 mL 30% H_2O_2.

Table 4.6 Dissolution of plutonium and uranium ceramic materials[a]

Material	Mineral Acids	Alkaline Fusion	Ammonium Bisulphate Fusion	High-Temperature/High-Pressure Dissolution
PuO_2	Dissolve in HNO_3/HF (dissolves with difficulty).	Sinter at 400°C[b] or fuse at 600°C[c] in 1:1 $Na_2O_2/NaOH$. Extract into HCl.	Fuse at 400°C[d] for 4 h. Extract into H_2SO_4.	
PuO_2/UO_2	Dissolve in 8*M* HNO_3, if in solid solution.		Fuse at 400°C[d] for 4 h. Extract into H_2SO_4.	
PuC, UC, and PuC/UC	Dissolve in mineral acids, (organic deposits are formed).	Fuse at 600°C[c] in 1:1 $Na_2O_2/NaOH$. Extract into mineral acid.	Ignite to oxide and treat as PuO_2/UO_2.[d]	
PuN	Dissolve in mineral acids.	Hydrolyzes readily in aqueous alkali.		
UN, PuN/UN	Dissolve $UN_{<1.5}$ in HCl/HF. (There is no loss of N_2.)			$UN_{<1.5}$ dissolve in HCl. $UN_{>1.5}$ dissolve in HCl/HF.

Note—See footnote at end of table.

Table 4.6 Dissolution of plutonium and uranium ceramic materials[a] (Cont'd)

Material	Mineral Acids	Alkaline Fusion	Ammonium Bisulphate Fusion	High-Temperature/High-Pressure Dissolution
	Dissolve $UN_{1.5}$ in HCl/HF in the presence of oxidizing agents. (There is some loss of N_2.)			
UP, U_3P_4	Dissolve in HCl/HNO_3. (There is loss of PH_3.)	Sinter at 350°C[c] in 3:1 Na_2O_2/Na_2CO_3. Extract into HNO_3		
USi	Dissolve in HCl/HF. (There is some loss of Si.)	Ignite to oxide, fuse with Na_2CO_3.[c] Extract with HCl.		
PuSi, PuSiC	Dissolve in HCl/HF. (There is some loss of Si.)	Ignite to oxide. Sinter in 1:1 Na_2O_2/NaOH.[b] Extract into HCl.		
(Pu,U)C-Fe	Dissolve in 8*M* HNO_3. Evaporate to fumes with H_2SO_4 to destroy organic residues.			

Note—See footnote at end of table.

Table 4.6 Dissolution of plutonium and uranium ceramic materials[a] (Cont'd)

Material	Mineral Acids	Alkaline Fusion	Ammonium Bisulphate Fusion	High-Temperature/High-Pressure Dissolution
(Pu,U)C-Mo	Dissolve in 6*M* HCl + HNO_3. (Organic residues are formed.)			
(Pu,U)C-Cr		Sinter at 400°C[b] with 1:1 Na_2O_2/NaOH. Extract in HNO_3.		
(Pu,U)C-Ce	Dissolve in 8*M* HNO_3. Evaporate to fumes with H_2SO_4.			
UC-Ru		Fuse at 600°C[c] in 1:1 Na_2O_2/NaOH.		

[a] From Ref. 70.
[b] Pt crucible.
[c] Al_2O_3 crucible.
[d] Pyrex vessel.
[e] Ni crucible.

Some of the more common ion-exchange, solvent-extraction, and precipitation methods that have been found useful for isolating U and Pu will be discussed. The separation chemistry of U is reviewed in References 71 and 72 and that of Pu in References 73, 74, and 75. A critical review of analytical separation methods applicable to reprocessing solutions will be found in Reference 76. The present discussion is based to a large extent on these earlier reviews.

4.5.1 Chemical Separation of Uranium

4.5.1.1 Ion-Exchange

Essentially all ion-exchange work has been performed with U in the hexavalent state. Uranium (VI) may occur in solution as cations or complex anions.

Uranyl ions can be adsorbed on cation exchangers from dilute sulfuric acid ($<0.5N$). However, most analytical separations on cation exchangers are performed under conditions conducive to anion formation for U so that the impurity elements are adsorbed while U passes through the column. Complex U anions are formed by the use of complexing agents such as acetate, chloride, fluoride, nitrate, sulfate, or carbonate. Adsorption on anion-exchange resins is strongest from dilute ($<0.1N$) H_2SO_4 or strong ($>6N$) HCl. Because Th is not adsorbed from HCl at any concentration, separation of U from Th is readily achieved. Tetravalent actinides are more strongly absorbed on anion exchangers from $6N$ HNO_3 than is U, and separations can be effected in that way.

Some representative methods for separating U from Th, Pu, or fission products are summarized in Table 4.7.

4.5.1.2 Solvent Extraction

Uranium (VI) can be selectively extracted from a nitrate medium with polar solvents. The extracted species is solvated undissociated uranyl nitrate. To prevent the dissociation of uranyl nitrate and to enhance the distribution coefficient of U, considerable quantities of Al, Ca, or ammonium nitrate (salting-out agents) are added to the aqueous solution. Sulphate and small amounts of phosphate and fluoride do not interfere In the presence of chloride, Fe(III) and other metals forming chloride complexes can be extracted. Various organic solvents have been used for extraction of the uranyl nitrate, including methyl ethyl ketone in carbon tetrachloride, mesityl oxide, ethyl acetate, tributyl phosphate (TBP) diluted in various organic solvents, and tri-*n*-octyl phosphine oxide (TOPO) in xylene or cyclohexane.

Table 4.7 Ion exchange methods for uranium separation

Exchanger	Solvent	Application	Ref.
	Cation Exchange		
Dowex AG-50W-X8	$1N\ H_2SO_4$	RE fission products, Th	77
Dowex 50-X8	90% tetrahydrofuran and 10% $6N\ HNO_3$	RE fission products, Th, Mo, Zr	78
Dowex 50	$1.5N\ HNO_3$	Pu(III)	79
Liquid cation exchange	$0.5N$ HCl	RE fission products, Th	80
Silica gel	Triethylene-tetramine-hexaacetic acid at pH = 5 to 6	Trace U from Th	81
Dowex 50		Th	82
	Anion Exchange		
Dowex 1-X8	80% methanol and 20% $6N$ HCl plus ascorbic acid	Th, Pu	83
Dowex 1	90% ethanol and 10% $5N\ HNO_3$	Th	84
Dowex 1-X8	90% methanol and 10% $6N$ HCl	Th	85
Dowex 1	$10N$ HCl	Th	86
Dowex 1-X8	$6N$ HCl	Th	87
De-Acidite FF	10 to $11N$ HCl plus HI	Pu	88
Dowex 1	$12N$ HCl	RE fission products, Th	89
Dowex 1-X8	80% methanol and 20% $5N\ HNO_3$	Th	90
Dowex 1-X8	90% dioxane and 10% $6N\ HNO_3$	Th	91
Dowex 1-X8	$1N\ HNO_3$	RE fission products, Th	92
Dowex 1-X8	$1.9M\ Al(NO_3)$ $0.1M\ HNO_3$, then $8M$ HCl	Al, Be, Mo, SS, Zr	93

RE = rare earth.

Currently, extraction with TBP is widely used. Although a number of elements, including Th and Pu, are also extracted, selection of proper extraction conditions can eliminate many interferences. For example, Pu interference is eliminated by reducing it to the trivalent state before extraction. The separation of U from Th is more efficient in HCl systems Extraction with TOPO is also used extensively, both from HNO_3 and HCl media.

Uranium (VI) has also been extracted from a nitrate medium with triphenylarsine oxide in chloroform (Ref. 94), and as the tetrapropylammonium uranyl nitrate complex into methyl isobutyl ketone (also known as MIBK or hexone) (Ref. 95). Some representative schemes for U separation by solvent extraction are listed in Table 4.8.

Table 4.8 Solvent-extraction methods for uranium separation

Aqueous	Organic	Application	Ref.
7*N* HCl	50% TBP in MIBK	Th	97
2*N* HCl	30% TBP in CCl_4	U and Pu from fission products for x-ray fluorescence analysis	98
Electrolyze in H_2SO_4; strip from organic with 7*N* HNO_3	1% cupferron in ether	RE fission products	99
EDTA, pH:4.1 to 6.5	Oxine in hexone	Irradiated Th	100
EDTA pH:2 to 3	2% diethyldithiocarbonate in pyridine	Th	101
0.1*N* ClO_4^-, pH:2	*N*-phenylbenzohydroxamic acid in chloroform	RE, Th	102
Nitrate, pH:2.0 to 2.3	*n*-butyric acid	RE, Th	103
3*N* HCl	0.1 *M* TOPO in cyclohexane	RE, Th, (Pu^{4+})	104
5*N* HCl	TBP	RE fission products, Th	105
3*N* HNO_3	Tetrapropylammonium in hexone	Fission products	95
1*N* HCl	TOPO in xylene	RE fission products, Th	106
EDTA, pH:2.5	TOPO in xylene	Th	107
6*N* HCl	Tri-iso-octylamine-2-nitropropane	From Th in HTGR dissolver solution	108
2*N* HNO_3, NaF, and sulfamic acid	TOPO in cyclohexane	Pu, others	109
HNO_3, $H_2C_2O_4$ and $Al(NO_3)_3$	Hexone	Mass spectrometric determination of U in HTGR dissolver solution	110

EDTA = (ethylenedinitrilo) tetraacetic acid; RE = rare earth.
TBP = tributylphosphate
MIBK = methylisobutyl ketone
TOPO = tri-n-octylphosphine oxide

4.5.1.3 Precipitation

Precipitation is infrequently used in U separation procedures largely because the methods have poor selectivity. Ion exchange and solvent extraction are more selective and are also easier to apply when work must be done in a glovebox or hot cell. Precipitation methods for separating U are reviewed in References 71 and 72.

Ammonia precipitates U(VI) quantitatively as the sparingly soluble diuranate, $(NH_4)_2U_2O_7$; but Th, Pu, and lanthanide fission products are also precipitated. If carbon dioxide has been absorbed from the atmosphere by the NH_4OH, some U may remain in solution because of the formation of a soluble carbonate complex. To avoid this, pyridine or hexamethylenetetramine are used as precipitants instead of ammonia.

The formation of a soluble uranyl carbonate complex has been used to mask U in the separation of numerous ions from U by hydroxide or carbonate precipitation. Vanadium, Be, and Th remain partly in solution together with the U.

4.5.2 Chemical Separation of Plutonium

4.5.2.1 Ion Exchange

The fact that Pu can exist in several valence states in solution allows more versatility in separation schemes for Pu than for U. Generally, adsorption on anion exchangers is strongest for Pu(IV), less so for Pu(VI), and least for Pu(III). This corresponds to the stability of the chloride and nitrate complexes of the three valence states. The Pu(IV) and Pu(VI) complex ions are strongly adsorbed from 6*N* HCl and 2*N* HNO_3. Little, if any, adsorption from HCl or HNO_3 at any concentration is observed for Pu(III). This fact is used to separate Pu from Th and U. If all three elements are adsorbed in an anion exchanger, Pu can be reduced to Pu(III) with HI or NH_4I and selectively eluted. To separate Pu from the rare earth fission products, oxidize to Pu(VI) and either adsorb the rare earths as cations or adsorb Pu on anion exchangers.

Plutonium can also be adsorbed on cation exchangers. Again, Pu(IV) is adsorbed most strongly, Pu(III), less so, and Pu(VI), least. Adsorption of Pu(III) and Pu(IV) is observed only at low concentrations (<1*N*) of H_2SO_4, HCl, and HNO_3. However, the acid concentration must not be too low, since hydrolysis or polymerization of Pu compounds will occur.

Representative ion-exchange methods for separating Pu from Th, U, or fission products are summarized in Table 4.9.

4.5.2.2 Solvent Extraction

Plutonium may be extracted from either chelate or ion-association extraction systems (Ref. 96). From an analytical chemistry viewpoint, thenoyltrifluoroacetone (TTA) is the most widely used chelating agent in solvent extraction systems, and tributyl phosphate (TBP)-nitrate and hexone-nitrate are the ion-association systems of importance. The complexes of Pu(IV) are the most stable and give the highest extraction yields. Complexes of Pu(VI) are less well extracted, and Pu(III) in general is not extractable.

Extractions are most often carried out from nitrate systems, since the efficiency is greater than from chloride systems. Anions such as fluoride, sulfate, phosphate, and other substances forming complexes more soluble in water than in organic solvents are to be avoided, since they inhibit extraction.

Thenoyltrifluoroacetone in organic solvents such as xylene or benzene, is a widely used extraction agent for tetravalent actinides.

The fact that Pu(III) is not extracted by TTA forms the basis for a purification procedure. Plutonium is separated from U by extraction of Pu(IV) from $0.75N$ HNO_3 or $1N$ HCl, while retaining uranium as UO_2^{2+}.

Americium and neptunium, present as Am(III) and Np(V) or Np(VI) in nitric acid solution, are not extracted by $0.5M$ TTA-xylene. If the organic phase is then washed with solutions that convert Pu to Pu(III), Pu can be selectively reextracted. Plutonium can be separated from Th by extracting Th(IV) after reduction of Pu to Pu(III). Separations of Pu from U and Th using other extraction systems such as TBP, hexone, or TOPO also rely on manipulation of the Pu valence.

Some representative extraction schemes for the separation of plutonium are summarized in Table 4.10.

4.5.2.3 Precipitation

In general, Pu is separated by precipitation only when present in small amounts, or if the sample consists of a pure solution of Pu. For the separation of trace amounts of Pu, coprecipitation techniques are used. The main criterion for selection of a carrier is that it must not interfere with the subsequent measurement of Pu. The carrier precipitates should be readily filterable and should be easy to redissolve. Coprecipitation with bismuth phosphate will separate Pu (and rare earth fission products) from U. Plutonium can be separated from the rare earths by oxidizing quantitively to Pu(VI) and reprecipitating the bismuth as the phosphate, which carries the insoluble fission product elements. Other carriers used for coprecipitation are discussed in References 72 and 73.

Numerous sparingly soluble Pu compounds have been used to isolate Pu from solutions of macro amounts of this element. Plutonium tetrafluoride is the most insoluble of these and is useful in separating Pu from U. Some other relatively insoluble compounds are the Pu(III) and Pu(IV) iodates (solubility: about 1.5 mg Pu/mL) and the peroxide $PuO_4 \cdot 2H_2O$ (solubility: 3.3 mg Pu/mL). The peroxide has been used to separate Pu from Am, which is not carried. A table of other sparingly soluble Pu compounds may be found in Reference 72, page 208.

4.6 REFERENCE MATERIALS FOR CHEMICAL ANALYSIS

All chemical methods for the determination of U and Pu require reference materials for calibration of the procedure and for measurement

Table 4.9 Ion-exchange methods for plutonium separation

Exchanger	Solvent	Application	Ref.
Cation exchange:			
$Zr_3(PO_4)_4$	0.5*N* HNO_3, 0.02*N* $NaNO_2$	U, fission products	111
Silica gel	4.5*N* HNO_3	U, fission products	112, 113
Dowex 50	0.25*N* HNO_3 0.025*N* hydroxylamine	U, fission products	114
Anion exchange:			
Dowex 1	9*N* HCl + SO_2	U(VI), Np(IV)	115
Dowex 1-X8	7*N* HNO_3	U, fission products	116
Dowex 1	12*N* HCl	Th	117
Dowex 1-X2	7.2*N* HNO_3	U and many others	118
AGMP-1	12*N* HCl	U, fission products, Am	119

Table 4.10 Solvent-extraction methods for plutonium separation

Aqueous	Organic	Applications	Ref.
0.5 to 1.5*N* HNO_3	0.5*N* TTA in xylene	RE fission products, U, Th	120
3*N* HNO_3	Tetrapropylammonium in hexone	Fission products	121, 122
2*N* HCl	30% TBP in CCl_4	U and Pu from fission products for X-ray fluorescence analysis	98
3*N* HNO_3	0.4*N* *N*-benzoylphenyl hydroxylamine in chloroform	From U fission products	123
6*N* HNO_3	0.1*N* TOPO in cyclohexane	RE fission products	124
11*N* NH_4NO + 5*N* HNO_3	Hexone	U	125

TTA = thenoyltrifluoroacetone; TBP = tributylphosphate; TOPO = tri-n-octylphosphine oxide; RE = rare earth.

control on a daily basis. Even "absolute" techniques, such as controlled-potential coulometry, require a single standard solution, prepared from a reference material, to verify the accuracy and precision of the method. The performance of a gravimetric technique should be regularly checked with a suitable reference material. Surface-ionization mass spectrometry, an "absolute" technique in which isotopic ratios are measured, requires standard reference material (SRM) or other reference materials for the determination of the mass discrimination bias factor and for the measurement control program.

In most analytical and plant control laboratories, two categories of reference materials are employed. The first category consists of standard or primary reference materials. These are stable materials characterized, certified, and distributed by a national or international standards body. In the United States, primary reference materials are offered for sale by NBS (Ref. 126) and NBL (Ref. 127) of the US Department of Energy. Plutonium and uranium reference materials available from these two organizations are listed in Tables 4.11 through 4.15. In addition to the materials listed, NBS also certifies several high-purity chemicals that are used as oxidation/reduction standards in the titrimetric determination of U and Pu. These chemicals are—

SRM 40	Sodium oxalate
SRM 83	Arsenic trioxide
SRM 136	Potassium dichromate

Additional primary reference materials are available from sources abroad (Ref. 128), such as the Central Bureau for Nuclear Measurements of the European Atomic Energy Community (EURATOM) Geel, Belgium, the Centre d'Etudes Nucleaires de Grenoble of the Commissariat a l'Energie Atomique (CEA) Grenoble, France, and the International Atomic Energy Agency (IAEA) Vienna, Austria.

The second category of reference materials consists of working reference materials (or working standards). They are materials that have been derived from primary reference materials or have been characterized against them. Working reference materials are used to monitor measurement methods, to calibrate and test methods and equipment, and to train and test personnel. A working reference material frequently is a product material of the plant that has been thoroughly homogenized and well characterized against a primary reference material.

Primary reference materials are relatively costly and are in limited supply. In addition, their composition may be quite different from that of material encountered in the plant. It is, therefore, desirable, if not necessary, for each laboratory to prepare and characterize working standards for daily use in the measurement control program. Guides for preparation and evaluation of working reference materials are available

Table 4.11 Plutonium and uranium assay standards available from NBS[a]

SRM	Assay Standard	Certified For—	Weight/Unit (g)	Purity (%)
945	Plutonium metal standard matrix	Impurities	5	99.9[b]
949f	Plutonium metal assay	Plutonium content	In preparation	
996	Plutonium-244 spike	Plutonium	In preparation	
950b	Uranium oxide	Uranium oxide	25	99.968 (U_3O_8)
960	Uranium metal	Uranium	26	99.975 (U)
993	Uranium-235 spike (solution)	Uranium	15	99.8195 (^{235}U)
995	Uranium-233 spike (solution)	Uranium	10	99.92 (^{233}U)

[a] From Ref. 126.

[b] Value is not certified, but is given for information only.

Table 4.12 Plutonium isotopic standards (plutonium sulfate tetrahydrate) available from NBS[a]

SRM	Weight/Unit (g)	Atom Percent				
		^{238}Pu	^{239}Pu	^{240}Pu	^{241}Pu	^{242}Pu
946	0.25	0.247	83.128	12.069	3.991	0.565
947	0.25	0.296	75.696	18.288	4.540	1.180
948	0.25	0.011	91.574	7.914	0.468	0.033

[a] From Ref. 126.

Table 4.13 Uranium isotopic standards available from NBS[a]

SRM	^{235}U Content of Uranium Oxide (U_3O_8)	Weight/unit (g)	Atom Percent			
			^{234}U	^{235}U	^{236}U	^{238}U
U-0002	Depleted	1.0	0.00016	0.01755	<0.00001	99.9823
U-005	Depleted	1.0	0.00218	0.4895	0.0046	99.504
U-010	Enriched	1.0	0.00541	1.0037	0.00681	98.984
U-015	Enriched	1.0	0.00850	1.5323	0.0164	98.443
U-020	Enriched	1.0	0.0125	2.038	0.0165	97.933
U-030	Enriched	1.0	0.0190	3.046	0.0204	96.915
U-050	Enriched	1.0	0.0279	5.010	0.0480	94.915
U-100	Enriched	1.0	0.0676	10.190	0.0379	89.704
U-150	Enriched	1.0	0.0993	15.307	0.0660	84.528
U-200	Enriched	1.0	0.1246	20.013	0.2116	79.651
U-350	Enriched	1.0	0.2498	35.190	0.1673	64.393
U-500	Enriched	1.0	0.5181	49.696	0.0755	49.711
U-750	Enriched	1.0	0.5923	75.357	0.2499	23.801
U-800	Enriched	1.0	0.6563	80.279	0.2445	18.820
U-850	Enriched	1.0	0.6437	85.137	0.3704	13.848
U-900	Enriched	1.0	0.7777	90.196	0.3327	8.693
U-930	Enriched	1.0	1.0812	93.336	0.2027	5.380
U-970	Enriched	1.0	1.6653	97.663	0.1491	0.5229

[a] From Ref. 126.

Table 4.14 Uranium and plutonium assay materials available from NBL[a]

No.	Type	Certified for—	Weight/Unit (g)	Uranium Content (Weight %)	^{235}U (Weight %)
17B	Uranium tetrafluoride	Uranium content, U(IV), UO_2 with some impurities	200	75.87	—
18	Uranium oxide (UO_3)	Uranium content, some impurities	500	82.10	—
97[b]	Uranium oxide (UO_2), enriched	Uranium, ^{235}U	25	87.705_8	2.382
112	Uranium metal, chips	Uranium, impurities	50	99.909	—
113[b]	Uranium hexafluoride (UF_6), enriched	Uranium, ^{235}U	5 to 10	67.580	1.7126
114	Uranium oxide (U_3O_8)	Uranium, impurities	50	84.73_9	—
115	Uranium metal, rod, depleted	Uranium, ^{235}U	75	99.97_7	0.2008
116[b]	Uranium metal, chunk, enriched	Uranium, ^{235}U	1.5	99.96_7	93.120
118[b]	Uranium-thorium carbide, multilayered fuel particle, coating consisting of pyrolytic carbon, bead form, enriched	Uranium, thorium, ^{235}U	10	13.38_8	93.095
119[b]	Uranium-thorium carbide, multilayered fuel particle, coating consisting of pyrolytic carbon and silicon carbide, bead form, enriched	Uranium, thorium, ^{235}U	15	7.12_8	93.095
120[b]	Uranium oxide (UO_2), enriched	Uranium, ^{235}U	50	87.35_5	1.349
122[b]	Plutonium oxide (PuO_2)	Plutonium content/isotopic	In preparation	—	—

[a] From Ref. 127.

[b] Special nuclear material, license required for purchase.

Table 4.15 Uranium isotopic and trace element materials available from NBL[a]

No.	Type	Certified For—	Weight/Unit (g)	$^{233}U/^{235}U$	$^{238}U/^{235}U$
117[b]	Uranium isotope mixture, solution	Atom ratio: $^{233}U/^{235}U$ and $^{238}U/^{235}U$	0.3	1.0078	1.0116
121	Uranium oxide (UO_2)	Impurity elements	In preparation	—	—
123 (1-7)	Uranium oxide (U_3O_8)	18 impurity elements	In preparation	—	—
124 (1-7)	Uranium oxide (U_3O_8)	24 impurity elements	In preparation	—	—

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[a] From Ref. 127.

[b] Special nuclear material, license required for purchase.

(Refs. 129 through 132). Clark and Jackson (Ref. 133) have described the preparation, handling, characterization, and packaging of uranyl nitrate solution for use as a working reference material.

A reference material should be analyzed daily or by each shift to ensure that the analytical method is under control. Process samples should not be analyzed until satisfactory results have been obtained on reference materials.

4.7 DETERMINATION OF URANIUM CONCENTRATION

4.7.1 Gravimetry: The Ignition Impurity-Correction Method

Description of Method

The ignition impurity-correction method is the most widely used gravimetric method for the determination of U in high-purity U compounds. In this method a weighed portion of the material is converted to U_3O_8 by ignition in air. The final weight of U_3O_8 is corrected for the nonvolatile impurities present as determined by spectrometric analysis. The oxide impurities are usually considered to be present in their highest valency state. Large sample weights (a minimum of 5 g) are required to minimize weighing errors.

High precision is easily attainable on a routine basis with this method when rigidly controlled conditions of ignition and regular periodic checks of performance are maintained. Other advantages of the method are low operator time per determination, no need for dissolution of oxide samples, and simplicity of the laboratory equipment required.

For the gravimetric method to produce accurate results, the final weighing form (U_3O_8) must have a stoichiometry that is well known and reproducible with high precision. According to Booman and Rein (Ref. 134) "the preparation of stoichiometric U_3O_8 depends on such factors as starting compound, surface area-to-volume ratio of the sample, temperature, and time for ignition." In addition, the partial pressure of oxygen in the atmosphere has been cited as a factor that could lead to variable results (Ref. 135). A number of investigators have studied the ignition conditions required to produce U_3O_8 of known and reproducible stoichiometry (Refs. 136 through 142). Some of these studies indicate that long ignition times are required to obtain stoichiometric U_3O_8.

For most analytical work, long ignition periods are not practical. Methods designed for routine analysis (Refs. 143 and 144) specify shorter ignition times and well-controlled ignition temperatures, but may not yield U_3O_8 of the theoretical stoichiometry. When the U content of the oxide formed under these conditions has been established by a precise potentiometric titration or a precise gravimetric procedure, the direct ignition method bias can be determined and applied to the results accordingly.

Bias may be determined by the gravimetric procedure developed by S. Kallman. The procedure, described in detail in Reference 145, is known to result in stoichiometric U_3O_8 as the final weighing form. The procedure is based on experiments that showed that substoichiometric or superstoichiometric U_3O_8 can be easily coverted to stoichiometric U_3O_8 by preheating these nonstoichiometric forms of U_3O_8 first in hydrogen for 15 to 20 min to form UO_2, and then heating in air at 850°C to form stoichiometric U_3O_8 (Ref. 146).

Kallman's results are corroborated by the thermogravimetric results of Gerdanian and Dodé (Ref. 138). They showed that substoichiometric $UO_{2.6622}$ (U_3O_8 = $UO_{2.6667}$) formed by heating U in air at 800°C, when reduced in oxygen-free hydrogen at 900°C, formed $UO_{2.0004}$. Subsequent reoxidation of this near-stoichiometric oxide in air at 800°C produced $UO_{2.6668}$.

Yamamura et al. (Ref. 147) favor the use of Kallman's method for routine use in the gravimetric determination of U. Weighing the nearly stoichiometric UO_2 formed by reduction with hydrogen is not recommended, since freshly reduced UO_2 shows considerable reactivity with the water and oxygen in air (Ref. 140).

It should be noted that the temperature for the final oxidation to U_3O_8 should not substantially exceed 900°C. Duval (Ref. 148) has stated that "dissociation of U_3O_8 to UO_2 begins to take place at 946°C and it is essential to keep below this temperature when heating in air or oxygen." This statement seems to be supported by Eberle and Lerner (Ref. 149), who found an increase over the theoretical value in the U(IV)/total U ratio when temperatures exceeding a few degrees below 900°C were employed.

Scope of Applications

The gravimetric method is applicable to the determination of U in pure product material, such as UF_6, uranyl nitrate solution, UF_4, and UO_2. It has been stated that for accurate results the total concentration of impurities should not exceed 500 $\mu g/g$ (Ref. 143). Gram quantities of material are required (5-g minimum) to minimize weighing errors.

Summary of Performance

Table 4.16 summarizes the performance of the method as applied to various feed, product, and scrap materials. The performance listed is either a single reported value or the unweighted average and range of several values for a specific material type. Results were combined within material type and reference category when no significant performance variations were observed even though different method variations may have been used in obtaining the results. Specific method applications are discussed later in this section, in paragraphs corresponding respectively to the literature, user, and exchange program source categories listed in the table.

Table 4.16 Summary of performance: gravimetric ignition impurity-correction method for uranium

Application	Performance (% RSD) Random Error	Performance (% RSD) Systematic Error	Source[a]
Feed and product material:			
UF_6	0.08	—	L
	0.039[b]	0.017	U
	(0.02 to 0.062)		
	0.038, 0.075	—	E
UF_4	0.02	—	L
	0.058	—	U
UO_2 powder, product and standard material	0.024[b]	0.014	U
	(0.008 to 0.059)	(0.001 to 0.023)	
	0.017	—	E
	(0.004 to 0.053)		
UO_2 pellets, product material	0.011[b]	0.015	U
	(0.004 to 0.025)		
	0.007	—	E
Clean scrap:			
U_3O_8 subblend, 75% U	2.2[b]	0.023	U
Clinkers, 75 to 85% U	8.3[b]	0.023	U
	(1.3 to 19)		
Hard scrap, 88% U	0.014[b]	0.023	U
Laser fines, 88% U	0.009[b]	0.023	U
Green pellets, 87% U	0.30[b]	0.023	U
Miscellaneous Scrap:			
UO_2 powder/pellets with $(NH_4)_2C_2O_4$, NH_4HCO_3; hard scrap	0.03 to 0.07	0.008	U
UO_2, U_3O_8	0.02	—	U
UNH	0.06	—	U
Low-level uranium solution, uranyl nitrate, 0.1 g U/g	0.08	—	L

UNH = uranyl nitrate solutions.

[a] E = survey of exchange programs; L = literature survey; U = users' survey of production facilities.

[b] Includes bulk sampling error.

Equipment

(1) Balance: analytical; single pan; capacity 150 to 200 g; 0.1-mg sensitivity, readability, and precision.

(2) Furnace: muffle, quartz-lined (or platinum-lined), capable of controlled temperatures in the range of 800°C to 900°C to within ± 20°C. The furnace temperature should be calibrated

using a technique such as that of Eberle and Lerner (Ref. 149). When UF_4 or UF_6 are to be analyzed, one may wish to use a pyrohydrolysis furnace. A description may be found in Reference 143, p. 413.

(3) Ignition crucibles: 30-mL platinum crucibles are generally used. For analysis of UF_6, 100-mL platinum boats are recommended (Ref. 144, method C 761).

Special apparatus required for the analysis of UF_6 is described in Reference 144, method C 761. Additional apparatus used in the reduction-with-hydrogen step of Kallman's method is listed and illustrated in Reference 145.

Major Sources of Error

Weighing errors resulting from the accuracy limits of the analytical balance, and nonstoichiometry of the U_3O_8 weighing form are the principle sources of error.

Nonvolatile impurities must be determined by a carrier distillation spectrographic method (see Ref. 144; Ref. 145, p. 5-2), and a correction applied to the weight of U_3O_8 obtained in the gravimetric determination. Concentrations of impurities should not total more than 500 μg/g for accurate results. It has been shown (Ref. 141) that calcium and phosphorus give high results in the U determination, especially if their concentrations exceed 1 mg/g. The presence of anions of phosphorus leads to the formation of uranyl pyrophosphate rather than U_3O_8.

Measurement Control Requirements

The performance of the direct-ignition gravimetric procedure should be checked periodically by using control standards or by analyzing the sample using the hydrogen reduction procedure. (See Ref. 145, p. 4-48.) Alternatively, the ignited U_3O_8 can be dissolved and analyzed using a precision titrimetric method. The method of Voss and Greene (Ref. 150) as modified by Vita, Trivisonno, and Walker (Ref. 151) has been recommended for this purpose. Detailed instructions for this method may be found in Reference 145, p. 4-33. The performance of the method should be checked for each different type of material to be analyzed.

Data Analysis Requirements

Calculate the number of grams of U per gram of sample using the following equation:

$$U_A = \frac{W(F - C)G}{S} \tag{4-13}$$

where

U_A = the U assay in grams of U per gram of sample

W = the number of grams of ignited oxide (sum of U and impurity oxides)
F = nonstoichiometry factor (ratio of stoichiometric uranium oxide plus impurity oxides determined by the hydrogen reduction method (Ref. 145) to the nonstoichiometric uranium oxide plus impurity oxides determined by the direct ignition method
C = the sum of the weights of the impurity oxides found by spectrometric analysis in grams per gram of total ignited oxide
G = gravimetric factor (U/U_3O_8) corrected for isotopic composition in grams U per gram U_3O_8
S = the grams of sample taken for analysis

Survey of Selected Literature

The gravimetric method has been applied to the analysis of several pure product materials, including U metal (but not powdered U metal), uranyl nitrate solution, UO_2, UO_3, UC_2, U_3O_8, UF_4, and UF_6. The procedure varies for each material. The following paragraphs will mention sources of specific procedures and give performance figures, when available.

Uranium Metal and Uranyl Nitrate Solution

Specific procedures are given in References 143 and 144, method C 799. In the latter procedure, hydrofluoric acid is added to obtain stoichiometric U_3O_8. Analysis of a uranyl nitrate solution of 0.1 g U/g by 14 laboratories (Ref. 152), using the method given in Reference 143, gave these results:

Bias (relative laboratory difference from prepared value)	+0.06%
Relative standard deviation within laboratories	0.08%
Relative standard deviation between laboratory averages	0.36%

UF_4

A specific procedure is given in Reference 143. The results (Ref. 152) on a sample of UF_4 from 14 laboratories showed:

Bias (relative laboratory differences from reference value)	−0.02%
Relative standard deviation within laboratories	0.02%
Relative standard deviation between laboratory averages	0.05%

UF_6

Specific procedures using pyrohydrolysis are given in References 143; 144, method C 761; and 153. In these procedures, the UF_6 contained in a P−10 tube is cooled with liquid nitrogen, then hydrolyzed in distilled water. The UO_2F_2 solution produced by the hydrolysis is evaporated to dryness, then converted to U_3O_8 by pyrohydrolysis at 850°C to 900°C. An evaluation (Ref. 152) in which several laboratories used this procedure gave the following results:

Bias (relative laboratory differences from reference value)	−0.15%
Relative standard deviation within laboratories	0.08%
Relative standard deviation between laboratory averages	0.06%

Survey of Production Facilities

The gravimetric ignition impurity-correction method is the method most commonly found at production facilities for determining U in pure U feed and product materials. The specific procedure used varies with the material analyzed. Three general procedure variations were found to apply to the different material types encountered:

(1) *UF_6:* A solidified sample is hydrolyzed in cool deionized water to UO_2F_2 and then evaporated to dryness. The dry UO_3 is converted to U_3O_8 by pyrohydrolysis at 850°C to 900°C for 2 to 4 h.

(2) *Powders:* Five- to 10-g samples are ignited in air at 900°C for 4 h.

(3) *Pellets:* Pellets are sized into small chunks, preheated at 500°C for 2 h, and then ignited in air at 900°C for an additional 2 h.

In addition to standard laboratory equipment, each method requires a temperature-controlled muffle furnace and Pt crucibles or boats. For those applications requiring a pyrohydrolysis step, a steam generator with furnace inlet is used.

Method performance is verified periodically by measuring standard reference materials or in-house working or control standards. NBL-97 UO_2 powder and NBL-113 UF_6 (see section 4.6 of this chapter) are materials most commonly used for this purpose. These measurements are normally made no less than twice each week the procedure is used.

Systematic errors are calculated by statistically combining the standard deviation of the mean determined from the replicate verification standard measurements and the total uncertainty of the standard's certified value. The histogram shown in Figure 4.2 presents the systematic errors associated with the measurement methods of various laboratories.

Random errors are determined from replicate measurement of process and standard materials. Normally the random error will include short-term systematic errors associated with day-to-day and operator-to-operator variations as these variations are considered to be part of the measurement method. In several cases, bulk sampling error is included as part of random error. This is because the particular sampling/analysis scheme used by a laboratory does not permit separating measurement and sampling errors. A discussion on sampling error is presented in section 4.3 of this chapter. The histogram in Figure 4.2 presents the random errors associated with the measurement methods of various laboratories. Except for three scrap categories (green pellets, U_3O_8-subblend, and clinkers), random errors vary between 0.005% and 0.07% RSD. Within that range, no difference can be seen between results with and without sampling error contributions.

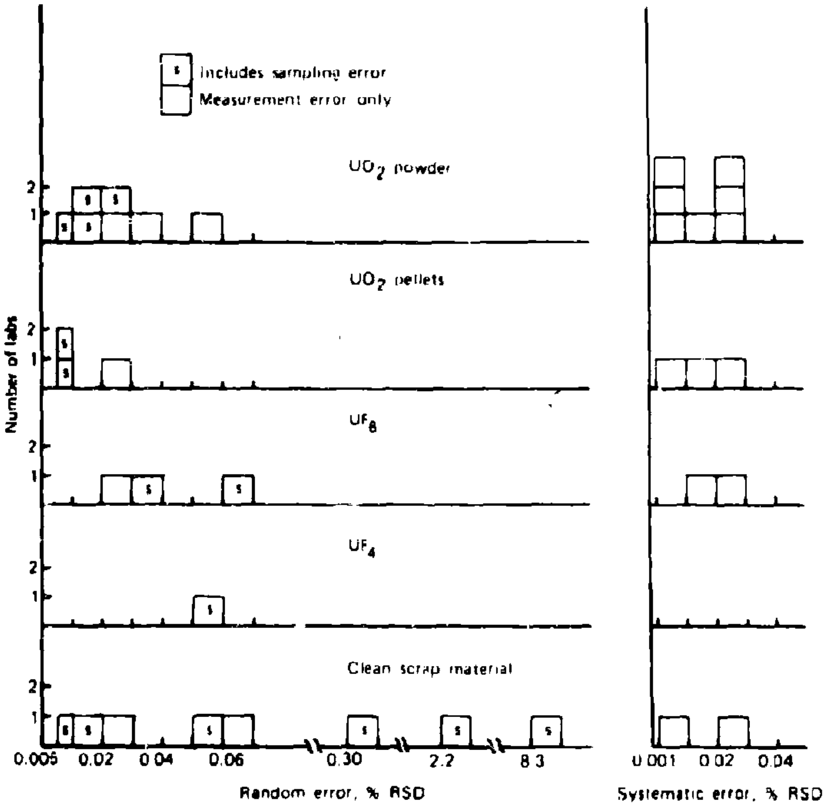

Figure 4.2 Performance of gravimetric ignition impurity-correction method for uranium—users' survey of production facilities.

Survey of Exchange Programs

The Safeguards Analytical Laboratory Evaluation (SALE) program participants use the gravimetric method to analyze uranyl nitrate solutions and UO_2 powder and pellet materials (Ref. 154). One to 5 g of U as UNH or 5 to 10 g of U as UO_2 are sampled for analysis. UNH solutions are dried and then converted to U_3O_8 by igniting in air at 850°C to 900°C. UO_2 powders are ignited directly and UO_2 pellets are either sized to small chunks or preheated at 500°C before igniting to U_3O_8.

The within laboratory unweighted average random errors for UO_2 powder, UO_2 pellets, and UNH are 0.017%, 0.007%, and 0.023% RSD, respectively. The histogram in Figure 4.3 presents a distribution of the performance values of the individual laboratories.

The General Analytical Evaluation (GAE) program participants use several variations of the basic gravimetric procedure for determining U in UF_6 (Ref. 155). An initial hydrolysis step is common to all procedures. The final ignition in air at 900°C is employed by all laboratories except one, which uses a pyrohydrolysis at 850°C to convert the sample to U_3O_8. One laboratory precipitates U as ammonium diuranate before drying and igniting to U_3O_8. The within laboratory unweighted average random error for eight laboratories using the different procedure variations is 0.038% RSD with a range of 0.018 to 0.082%. The histogram in Figure 4.3 presents the distribution of the individual laboratory performance values.

4.7.2 Reduction-Oxidation Titrimetry: The Davies and Gray/NBL Method

Description of Method

Among the many methods proposed for the accurate assay of U in nuclear materials, the titrimetric method of Davies and Gray (Ref. 156) as modified by workers at NBL (Ref. 157) has emerged as the most selective and hence the most versatile technique.

The original method of Davies and Gray (Ref. 156) involved the reduction of hexavalent uranium to the tetravalent state by ferrous ion in a concentrated phosphoric acid solution containing sulfamic acid, oxidation of the excess Fe(II) with nitric acid in the presence of Mo(VI) catalyst, dilution of the solution, and then titration of the U(IV) with potassium dichromate to a visual end point. Barium diphenylamine sulfonate was used as the indicator. The original method suffered from a sluggish end point. At NBL this method was extensively studied and improved by the addition of a small amount of V(IV) to the solution before titration to accelerate the attainment of equilibrium (Refs. 157 and 158). This modification made possible the use of potentiometric detection of the end point and adaptation of the method for use with automatic titration equipment (Refs. 157 and 159). The basic procedure has also been extended to a coulometric titration (Ref. 160) in which the titrant is V(V) electrogenerated at constant current by the oxidation of V(IV). The coulometric titration has also been automated (Ref. 161), and factors affecting the automated titration have been studied (Ref. 162).

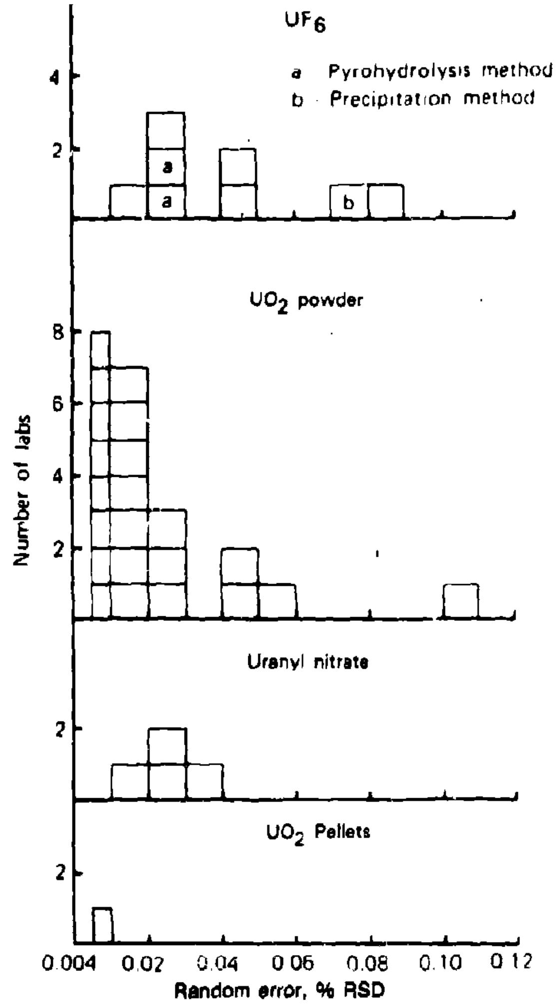

Figure 4.3 Performance of gravimetric ignition impurity-correction method for uranium—survey of exchange programs.

The principal steps and chemical reactions involved in the potentiometric version of the Davies and Gray/NBL method are the following:

(1) Sampling
(2) Dissolution
(3) Pretreatment to remove interferences, if required (e.g., fuming with sulfuric acid)

(4) Reduction of U(VI) to U(IV) with Fe(II) in H_3PO_4-sulfamic acid medium:

$$\mathrm{U(VI)} + \mathrm{Fe(II)} \xrightarrow[\mathrm{NH_2SO_3H}]{\mathrm{H_3PO_4}} \mathrm{U(IV)} + \mathrm{Fe(III)} + \underset{\text{excess}}{\mathrm{Fe(II)}} \qquad (4\text{-}14)$$

(5) Destruction of excess Fe(II) by molybdate-catalyzed nitrate oxidation:

$$\mathrm{Fe(II)} + \mathrm{HNO_3} \xrightarrow[\mathrm{NH_2SO_3H}]{\text{Mo(VI) catalyst}} \mathrm{Fe(III)} + \mathrm{NO}_x + \mathrm{N_2} \qquad (4\text{-}15)$$

(6) Dilution of sample with 1*M* H_2SO_4 and titration of U(IV) to U(VI), in the presence of vanadium catalyst, to a potentiometric (Pt-calomel) equivalence point:

$$\mathrm{U(IV)} + \mathrm{Cr(VI)} \xrightarrow{\text{V(IV) catalyst}} \mathrm{U(VI)} + \mathrm{Cr(III)} \qquad (4\text{-}16)$$

Strict adherence to a number of procedural details is required to obtain accurate results with this method. A discussion of these details is given in Reference 42. Step-by-step procedures may be found in References 158 and 42.

Scope of Applications

The Davies and Gray/NBL method employing a potentiometric end point (Ref. 158) is applicable to a variety of U solutions containing nitric, sulfuric, and perchloric acids and to solutions containing several constitutents that interfere in other high-precision U methods. Solutions analyzed may be derived from the dissolution of uranium oxide, uranium metal, uranium salts, uranium alloys, and such samples as nuclear fuels clad with aluminum, stainless steel, or zircaloy. The original Davies and Gray titration using a visual end point (Ref. 156) is still occasionally used for the analysis of uranyl nitrate solution and uranium dioxide powder (Ref. 154).

Summary of Performance

Table 4.17 summarizes the performance of the method as applied to various feed, product, and scrap materials. Two method variations are employed, the basic Davis and Gray visual end point method and the NBL modified method for potentiometric end point detection. A third high-precision method is used in one application.

Table 4.17 Summary of performance: Davies and Gray titrimetric method for uranium

Application	Method[a]	Performance (% RSD) Random Error	Performance (% RSD) Systematic Error	Source[b]
Uranium metal, alloys:				
Metal	NBL	"No bias"		L
Metal, standard material	NBL	0.06	0.018	U
Metal particles, TRIGA feed	NBL	0.06[c]	0.017	U
Metal, 99.9% U	NBL	0.004	—	E
Alloy material	—	<0.04 (bias)		L
TRIGA alloy standard material	NBL	0.06	0.018	U
TRIGA alloy process material	NBL	0.65[c]	0.018	U
UAl_x	NBL	0.074[c]	0.018	U
UF_6	NBL	0.28	—	E
U_3O_8: powder, standard material	NBL	0.091, 0.12	0.034, 0.040	U
	Visual	0.12 (0.048 to 0.20)	0.032	U
UO_2:				
Powder, product and standard material	NBL	0.11	0.035	U
	NBL	0.046 (0.004 to 0.11)	—	E
	Visual	0.078, 0.56	—	E
	Visual	0.26[c]	0.034	U
HTGR feed: UO_2, U_3O_8, $(U,Th)O_2$ powder	NBL	0.89[c]	0.017	U
Uranium carbide	Visual	0.22[c]	0.034	U

Note—See footnote at end of table.

Table 4.17 Summary of performance: Davies and Gray titrimetric method for uranium (Cont'd)

		Performance (% RSD)		
Application	Method[a]	Random Error	Systematic Error	Source[b]
Uranium solutions:				
Pure solutions	NBL	0.07 (0.02 to 0.15)	—	L
	HP	0.003 to 0.008	—	L
Standard solution, 319 g U/L	NBL	0.07	—	U
Standard solution, 20 g U/L	NBL	0.10^c	0.060	U
Uranyl nitrate	NBL	0.060 (0.009 to 0.15)	—	E
	Visual	0.14, 0.07	—	E
Uranium/thorium carbide:				
HTGR process material	NBL	0.07 to 0.28^c	0.017	U
SiC-coated standard material	NBL	0.62	0.53	U
SiC-coated process material	NBL	0.2 to 3^c	0.53	U
Uranium/plutonium dioxide:				
Powder	NBL	0.17, 0.31	—	E
Pellets	Visual	0.29^c	0.034	U
Uranium/plutonium carbide:	Visual	0.45^c	0.034	U
Clean scrap:				
Green pellets, 84% U	NBL	3.1^c	0.035	U
Green scrap, 86% U	NBL	1.0^c (0.32 to 1.4)	0.035	U

Note—See footnote at end of table.

Table 4.17 Summary of performance: Davies and Gray titrimetric method for uranium (Cont'd)

Application	Method[a]	Performance (% RSD)		Source[b]
		Random Error	Systematic Error	
U_3O_8 scrap blends	NBL	0.85[c]	0.071	U
UO_2 scrap, 81.7% U	Visual	0.076	0.028	U
Miscellaneous scrap:				
Recycle fines, U metal	NBL	0.34[c]	0.018	U
Raw stock scrap, U metal	NBL	2.3[c]	0.013	U
UAl_x scrap, 70% U	NBL	0.25 to 12[c]	0.018	U
$ADU/UO_2/U_3O_8$, 67% to 80% U	NBL	7.2[c] (2.4 to 10)	0.035	U
UO_2 powder, Gd_2O_3, $(NH_4)_2C_2O_4$, NH_4HCO_3, wet/dry sludge, ADU, ash	Visual	4.4	0.037	U
UO_2, Gd_2O_3 pellets and hard scrap	Visual	2.0	0.037	U
TRIGA waste: alloy, hydride, oxide	NBL	2.6[c]	0.018	U
ADU, dry, 70% to 75% U	NBL	3.5[c] (0.69 to 4.8)	0.035	U
ADU, wet, 50% U	NBL	19[c]	0.035	U
Dirty scrap:				
Floor sweepings, UO_2, 60% to 80% U	NBL	13[c] (4.8 to 19)	0.035	U
Grinder sludge, UO_2, dry, 73% to 85% U	NBL	5.3[c] (0.31 to 18)	0.035	U
Grinder sludge, UO_2, wet, 76% to 82% U	NBL	5.0[c] (2.7 to 7.8)	0.035	U

Note—See footnote at end of table.

Table 4.17 Summary of performance: Davies and Gray titrimetric method for uranium (Cont'd)

Application	Method[a]	Performance (% RSD)		Source[b]
		Random Error	Systematic Error	
Contaminated scrap, UO_2, 57% to 78% U	NBL	30[c] (3.5 to 39)	0.035	U
Small press, 52% to 75% U	NBL	23[c] (9.5 to 31)	0.035	U
Ash, 31% U	NBL	19[c]	0.053	U
Calcined scrap	NBL	9.1[c]	0.071	U
Low-level uranium solutions:				
UNH solution, 0.1 g U/g	NBL	13[c]	0.035	U
UNH waste, scrap	Visual	0.33	0.037	U
	NBL	0.24[c]	0.071	U
UNH, raffinate, UO_2F_2, miscellaneous aqueous/organic solutions	NBL	0.63[c]	0.071	U

ADU = ammonium diuranate; UNH = uranyl nitrate solutions; TRIGA = training reactor, isotopes production, General Atomic; HTGR = high-temperature gas reactor

[a] HP = high-precision method (several-gram sample size plus solid titrant addition); NBL = New Brunswick Laboratory potentiometric end point method; Visual = visual end point method.

[b] E = survey of exchange programs; L = literature survey; U = users' survey of production facilities.

[c] Includes sampling error.

The performance listed is normally a single reported value for a particular, usually unique, material type. Some values are reported as unweighted averages and a range of the performances of different laboratories on similar materials. Other values are reported as a weighted average and a range, or as a range only, of the performance of a single laboratory. Specific method applications are discussed later in this section in paragraphs corresponding to the literature, user, and exchange program source categories listed in the table.

Equipment

The apparatus required for the basic Davies and Gray/NBL procedure is the following:

(1) Balance. Analytical; single pan; capacity 150 to 200 g; 0.01-mg sensitivity, readability, and precision
(2) pH meter. Wide-scale, analog-type
(3) Reference electrode, calomel. Asbestos-fiber, ceramic-frit, cracked-glass, or other low-leakage type junction
(4) Platinum indicator electrode. Wire-type sealed in glass or coil of sturdy wire
(5) Buret. 50 or 100 mL, with bulb reservoir
(6) Small scoop. For delivering 125 ± 25 mg of vanadyl sulfate dihydrate crystals

The approximate cost of this apparatus will be $2000 to $4000 depending largely on the quality of the balance and the pH meter.

Automation of the potentiometric titration (Refs. 157 and 159) or coulometric titration (Refs. 163 and 164) has included use of a Fisher Scientific Co. Titralyzer. Such automation can add another $11,000 to $13,000 in cost. A fully automatic titration system, such as the Lawrence Livermore Laboratory computer-controlled system described in Reference 161, is estimated to cost $50,000 to duplicate. The advantage of such advanced systems is the ability to analyze automatically many samples each day.

Major Sources of Error

Errors most commonly encountered result from

(1) Accuracy uncertainty of the analytical balance
(2) Uncertainty in the assay of the potassium dichromate
(3) Change in titer of the standard potassium dichromate solution
(4) Malfunctioning of the platinum indicator electrode
(5) Inadequate operator techniques

The interferences associated with this method have been studied in great detail. Most elements in the periodic table have been tested experimentally as potential interferents. Figure 4.4, taken from Reference 165, summarizes the results of the interference studies completed at NBL. By definition, an element is considered an interferent if its presence in a concentration of 15% or less of the U present introduces an analysis error (bias) greater than 0.1% relative. Unmarked squares on the chart indicate elements that do not interfere. A bullet and an "E" indicate elements that interfere and which must be removed from the sample before titration. A bullet and a "T" indicate elements that interfere under some circumstances but require only a simple pretreatment to prevent adverse effects. Such treatments include fuming with sulfuric acid or perchloric acid, and preoxidation with potassium dichromate. Interfering substances and methods for their removal or control are as follows (Ref. 165):

Element	Treatment
Mo, Tc, Ru, Os, Cl, Br, and large excesses of F	Fume sample aliquot in 3 to 5 mL $HClO_4$ and/or H_2SO_4
I	Add bromine water, evaporate, fume in $HClO_4$ or H_2SO_4
As, Sb, Sn	Add small amount of $K_2Cr_2O_7$ to sample aliquot prior to Fe(II) reduction step
V, Mn, Mo, Ru, Pd, Ag, Os, Ir, Pt, Hg, As, Sn, Sb, Cl, Br	TBP extraction in CCl_4. Kerosene interferes, causing results low by 20% to 40% and cannot be used as a solvent for TBP in this application. Cyclohexane is a satisfactory substitute for CCl_4
10% Au	Reduce to metal and separate

A technique for removing nearly all interfering elements from samples consists of converting the sample to solution form in 4 to 5*N* nitric acid and extracting the U with 30% TBP in CCl_4. Elements that can be removed in this manner are marked with an "E" in Figure 4.4. The only interfering elements not effectively removed by the extraction are I, Tc, and Au. The carbon tetrachloride-TBP phase from the extractions may subsequently be titrated in the same manner as an aqueous sample with the same high precision and accuracy.

The effects of nitrate and Mo are interdependent. If present together in sufficient quantities, they interfere by causing the Fe(II) to be oxidized before all the U(VI) has been reduced to U(IV). The remedy is to reduce the nitrate concentration to a harmless level by light fuming of the sample solution with sulfuric acid (Ref. 157).

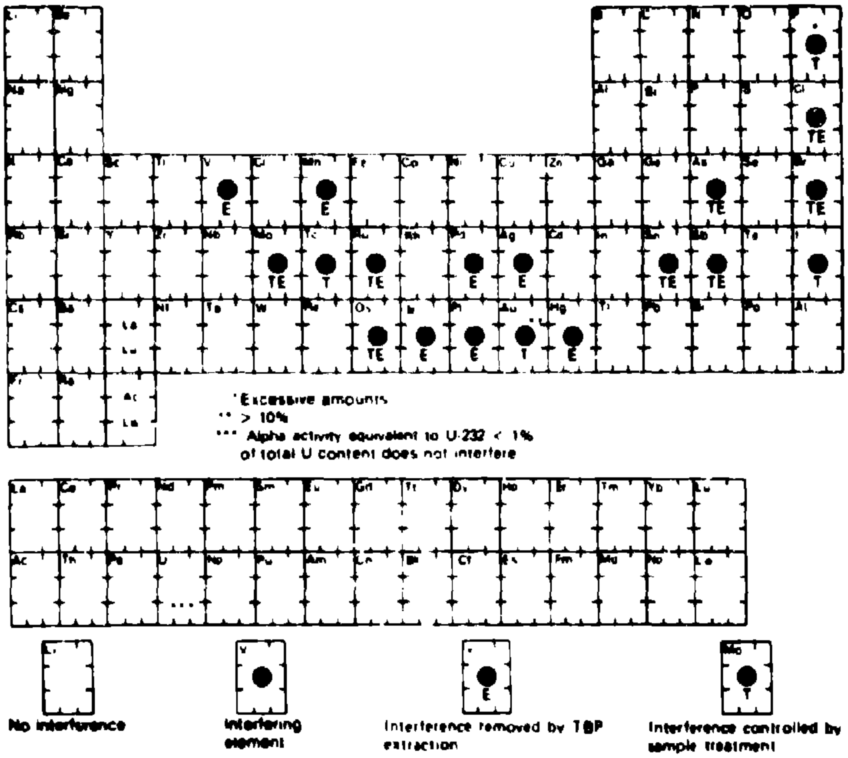

Figure 4.4 Interferences in the Davies and Gray/NBL titrimetric method for uranium.

Measurement Control Requirements

At least two portions of a working calibration and test material traceable to NBS measurements should be analyzed each day, and the results should agree with the established value within 0.05%. The procedures used should be the same as those used for the samples. Guidance on the preparation and evaluation of working calibration and test materials has been published (Refs. 42 and 132). The measurement control program in use at NBL is described in Reference 166.

Data Analysis Requirements

Calculate the amount of U in the sample as follows:

$$U = \frac{(NV + 6WA/M)\ [(\text{atomic weight of U})/2]}{\text{weight of sample, g}} \qquad (4\text{-}17)$$

where the atomic weight of U has been corrected for isotopic composition and where

U = grams of U per gram of sample
N = normality of potassium dichromate titrant
V = volume of potassium dichromate titrant used, liters (corrected for ambient temperature changes, if necessary)
W = weight of solid potassium dichromate added (high-precision method only), corrected for air buoyancy, grams
A = purity of potassium dichromate given in the NBS certificate, %/100
M = molecular weight of potassium dichromate, 294.19 g/mole

Survey of Selected Literature

The Davies and Gray/NBL method is applicable to a broad spectrum of sample types, as previously stated. Some of the materials that have been analyzed at NBL and preliminary treatment are as follows (Ref. 165):

Material	Treatment
U, UO_3, U_3O_8, UF_4	Dissolve in HNO_3, fume sample aliquots with H_2SO_4.
UO_2 powders and pellets, ADU, wastes, UO_2-ThO_2	Dissolve in HNO_3; filter; fuse residue in $NaHSO_4$ or Na_2CO_3; combine solutions.
Ore concentrates	Dissolve in HNO_3; fume sample aliquots with H_2SO_4 and HF.
HTGR fuel beads: (SiC-coated, pyrolytic carbon-coated, U-Th carbide)	(1) Ignite to remove carbon; fuse with Na_2CO_3; dissolve cake and fume with H_2SO_4 and HF to remove silica; precipitate U with NH_4OH to remove excess fusion salts; dissolve residue in HNO_3; fume sample aliquots with H_2SO_4. (2) Ignite to remove carbon; treat with Cl_2 at 900°C to decompose SiC; ignite as in (1), dissolve as with UO_2-ThO_2.
UC, UC_2	Ignite; dissolve in HNO_3; fuse any residue; fume sample aliquots with H_2SO_4.
U-Al, U-Si, UO_2-SS	Dissolve in HCl-HNO_3; fume with $HClO_4$; filter; volatilize silica with HF; fuse remaining residue with Na_2CO_3; fume sample aliquots with $HClO_4$.

Fissium alloy, fissium dross	Dissolve in HCl-HNO_3; treat residue with $NaOCl$ and $NaOH$; acidify with HCl; combine solutions; fume sample aliquots with $HClO_4$. (Residue from dross requires fusion with $NaOH$).
Ash samples	Fuse with Na_2CO_3-$NaNO_3$ (5:1) and/or $NaHSO_4$; dissolve cake in HNO_3-$HClO_4$; volatilize silica with HF; fume with $HClO_4$; fume sample aliquots with H_2SO_4.
UO_2-ZrO_2-Nb-Zr, UO_2-BeO	Dissolve in HNO_3-HF; fume sample aliquots with H_2SO_4 or $HClO_4$. (Large quantities of Nb may be removed by precipitation with SO_2.)
Dissolver solutions, organic solutions, wastes	Homogenize and reconstitute multiphase mixtures where necessary; destroy organics with hot H_2SO_4-HNO_3; fume sample aliquots with H_2SO_4.
U-Zr	Dissolve in HF; fume sample aliquots with H_2SO_4 or $HClO_4$.

With regard to the analysis of HTGR recycle fuel samples, the effects of high-energy alpha activity and technetium on the method have been investigated (Ref. 167). It was found that technetium was a serious interference when present in amounts from 1 to 15 mg in solutions containing 100 mg U. However, the interference could be removed by evaporating the test solution to dryness and flaming the walls of the titration vessel with a Bunsen burner to volatilize all of the Tc. In a test of the effect of high-energy alpha radiation, ^{244}Cm was substituted for ^{232}U. The presence of up to 4 mCi of ^{244}Cm produced no interference.

NBS standard reference materials/NBL ingot uranium metal

The performance of the basic Davies and Gray/NBL method has been extensively studied at NBL and elsewhere. In assays of NBS reference material and NBL ingot U metal, the method has been shown (Refs. 157, 168, and 169) to give results without bias.

Uranium alloys

When a variety of U alloys was ana[illegible] 157), a bias ranging from zero to 0.04% relative was found.

Uranium solutions

With samples containing 100 to 300 mg of U, the within-laboratory relative standard deviation of a single determination for the basic procedure is in the range of 0.02% to 0.05% (Refs. 157, 170, and 171).

Pietri, Paller, and Bingham (Ref. 165) reported recently that *under routine conditions* U can be measured without bias to a precision of 0.08% relative standard deviation for samples containing more than 50 mg U and to 0.15% RSD for samples containing 15 to 50 mg U.

The high-precision procedure, using weighed potassium dichromate and several-gram quantities of U, has been reported to yield a relative standard deviation of 0.003% to 0.008% (Refs. 168 and 171).

Slanina and co-workers (Ref. 172) have described the potentiometric titration of 2- to 25-mg amounts of U. During the sample preparation the walls of the titration vessels are cleaned by centrifugation. To avoid overshoot at the end point of the titration, a special differentiator is employed that interrupts the titration until equilibrium is reached. A bias of less than 0.04% relative and a relative standard deviation of 0.02% are claimed.

The method of Reeder and Delmastro (Ref. 173) extends the work of Slanina et al. (Ref. 172). A preprogrammed calculator controls the delivery of titrant so that the end point is approached as rapidly as possible, but only small increments of titrant are delivered near the equivalence point. Special attention is paid to temperature control at several critical steps. A bias of less than 0.05% relative and a relative standard deviation of 0.05% or better are claimed.

Survey of Production Facilities

The Davies and Gray titrimetric method is the method most commonly found at production facilities for determining U in materials of lower purity than can be accurately analyzed by the gravimetric method. This includes most materials in the various scrap categories.

Two method variations are employed by the different user facilities. These are the basic Davis and Gray visual end point method and the NBL modified method for potentiometric end point detection. These methods are described in more detail in "Description of Methods" in this Section and in References 156 and 157. Standard laboratory equipment, including a pH/mV meter with platinum and calomel electrodes, is used for the NBL modified method. The barium salt of diphenylamine sulfonic acid is used as the visual indicator in the basic method.

Method performance is verified periodically by measuring standard reference materials or in-house working or control standards. NBS U_3O_8 powder (NBS 950) or U metal (NBS 960) are the materials most commonly used for this purpose, either directly or as a means of establishing traceability for working or control standards. These measurements are normally made daily but not less than twice each week the procedure is used.

Systematic errors are calculated by statistically combining the standard deviation of the mean determined from the replicate verification standard measurements and the total uncertainty of the standards certified value. Table 4.18 lists the systematic error associated with the measurement methods of various laboratories.

Table 4.18 Performance of the Davies and Gray titrimetric method for uranium—users' survey of production facilities

		Performance (% RSD)	
Application	Method[a]	Random Error	Systematic Error
Uranium metal, alloys:			
Metal, standard material	NBL	0.06	0.018
	NBL	0.062	0.017
Metal particles, TRIGA feed	NBL	0.06[b]	0.017
TRIGA alloy, standard	NBL	0.06	0.018
TRIGA alloy, process material	NBL	0.65[b]	0.018
UAl_x	NBL	0.074	0.018
U_3O_8: powder, standard material	NBL	0.12	0.040
	NBL	0.091	0.034
	Visual	0.10	0.037
	Visual	0.048	0.028
	Visual	0.2	—
UO_2:			
Powder, product and standard material	NBL	0.11	0.035
	Visual	0.26[b]	0.034
HTGR feed: UO_2, U_3O_8, $(U,Th)O_2$	NBL	0.89[b]	0.017
Uranium carbide	Visual	0.22[b]	0.034
Uranium solutions:			
Standard solution, 319 g U/L	NBL	0.07	—
Standard solution, 20 g U/L	NBL	0.10[b]	0.060
Uranium/thorium carbide:			
HTGR process material	NBL	0.07 to 0.28[b]	0.017
SiC-coated standard material	NBL	0.62	0.53
SiC-coated process material	NBL	0.2 to 3[b]	0.53
Uranium/plutonium dioxide: Pellets	Visual	0.29[b]	0.034
Uranium/plutonium carbide:	Visual	0.45[b]	0.034
Clean scrap:			
Green pellets, 84% U	NBL	3.1[b]	0.035
Green scrap, 86% U	NBL	1.0 (0.32 to 1.4)[b]	0.035
U_3O_8 scrap blends	NBL	0.85[b]	0.071
UO_2 scrap, 81.7% U	Visual	0.076	0.028
Miscellaneous scrap:			
Recycle fines, U metal	NBL	0.34[b]	0.018
Raw stock scrap, U metal	NBL	2.3[b]	0.018
Sweepings, UAl_x, 70% U	NBL	0.38[b]	0.018
Button scrap, UAl_x, 70% U	NBL	0.39[b]	0.018
Briquette scrap, UAl_x, 70% U	NBL	0.25[b]	0.018
Recycle scrap, UAl_x, 70% U	NBL	0.47[b]	0.018
Crush line scrap, UAl_x, 70% U	NBL	1.4[b]	0.018
Compact line/debur scrap, UAl_x, 70% U	NBL	5.6[b]	0.018

Note—See footnote at end of table.

Table 4.18 Performance of the Davies and Gray titrimetric method for uranium — users' survey of production facilities (Cont'd)

Application	Method[a]	Performance (% RSD) Random Error	Performance (% RSD) Systematic Error
Furnace scrap, UAl_x 70% U	NBL	12[b]	0.018
$ADU/UO_2/U_3O_8$, 67% to 80% U	NBL	7.2 (2.4 to 10)[b]	0.035
UO_2 powder, Gd_2O_3, $(NH_4)_2C_2O_4$, NH_4HCO_3, wet/dry sludge, ADU, ash	Visual	4.4	0.037
UO_2 with Gd_2O_3 pellets and hard scrap	Visual	2.0	0.037
TRIGA waste: alloy, hydride, oxide	NBL	2.6[b]	0.018
ADU, dry, 70% to 75% U	NBL	3.5 (0.69 to 4.8)[b]	0.035
ADU, wet, 50% U	NBL	19[b]	0.035
Dirty scrap:			
Floor sweepings, UO_2, 60% to 80% U	NBL	13 (4.8 to 19)[b]	0.035
Grinder sludge, UO_2, dry, 73% to 85% U	NBL	5.3 (0.31 to 18)[b]	0.035
Grinder sludge, UO_2, wet, 76% to 82% U	NBL	5.0 (2.7 to 7.8)[b]	0.035
Contaminated scrap, UO_2, 57% to 78% U	NBL	30 (3.5 to 39)[b]	0.035
Small press, 52% to 75% U	NBL	23 (9.5 to 31)[b]	0.035
Ash, 31% U	NBL	13[b]	0.035
Ash, 30% U	NBL	24[b]	0.071
Calcined scrap	NBL	9.1[b]	0.071
Low-level uranium solutions:			
UNH solution, 0.1 g U/g	NBL	13[b]	0.035
UNH waste, scrap	Visual	0.33	0.037
	NBL	0.24[b]	0.071
UNH, raffinate, UO_2F_2, miscellaneous aqueous/organic solutions	NBL	0.63[b]	0.071

[a] NBL = New Brunswick Laboratory potentiometric end point method; Visual = visual end point method.

[b] Includes sampling error.

Random errors are determined from replicate measurement of process and standard materials. Normally the random error will include short-term systematic errors associated with day-to-day and operator-to-operator variations, as these variations are considered to be part of the measurement method. In several cases bulk sampling error (inhomogeneity) is included as part of random error. This is because the particular sampling/analysis scheme used by a laboratory does not permit separating measurement and sampling errors. A discussion of inhomogeneity is presented in Section 4.3 of this chapter. Table 4.18 lists the random errors associated with the measurement methods of the various laboratories.

Survey of Exchange Programs

The SALE program participants use the Davies and Gray titrimetric method to analyze UO_2 powder, UNH, and $(U,Pu)O_2$ powder (Ref. 154).

The basic method employing diphenylamine sulfonate visual indicator is applied only to UO_2 powder and UNH. The NBL modified method is applied to all three materials.

Little performance data are available for UO_2 and UNH by the basic method and for $(U,Pu)O_2$ by the NBL method. The histogram in Figure 4.5 presents the individual within-laboratory random error values that have been reported. Within laboratory unweighted average random errors for UO_2 powder and UNH by the NBL method are 0.046 and 0.060% RSD, respectively. The histogram presents a distribution of the individual laboratory performance values from which these averages were calculated.

The GAE program participants use the NBL modified method for determining U in UF_6 (Ref. 155). Again, the performance data are minimal and are presented in the Figure 4.5 histogram.

Only one participant in the uranium metal exchange program (Personal communication with J. W. Charles, Jr., Oak Ridge Y-12 Plant, Nov. 1980) uses the Davies and Gray titrimetric method. The performance of the NBL modified method for U metal at this laboratory is presented in the Figure 4.5 histogram.

4.7.3 Alternative Methods by Redox Titrimetry

The Davies and Gray/NBL method is the most widely used of the redox methods for the determination of U. There are, however, several other methods that are used for specific applications. Three of the more widely used methods are summarized in the following paragraphs. Alternative methods that are of historical interest can be found in References 1, 4, 9, and 10.

Description of Method

Jones Reduction/Dichromate Titration Method

The following method description is taken from Reference 174 where a detailed procedure will be found. The determination consists of (1) passing the sample solution through a 2% Zn amalgam (Jones reductor) to reduce the U(VI) to U(III) and U(IV), (2) aerating the solution to oxidize U(III) to U(IV), (3) adding an accurately weighed slight excess of primary standard potassium dichromate, and (4) titrating the excess dichromate with standard ferrous ammonium sulfate. The chemical reactions are

$$\mathrm{U(VI)} \xrightarrow{\text{Zn amalgam}} \mathrm{U(III)} + \mathrm{U(IV)} \qquad (4-18)$$

$$\mathrm{U(III)} \xrightarrow{\text{Air}} \mathrm{U(IV)} \qquad (4-19)$$

$$\mathrm{U(IV)} + \underset{\text{excess}}{\mathrm{Cr(VI)}} \longrightarrow \mathrm{U(VI)} + \mathrm{Cr(III)} + \underset{\text{excess}}{\mathrm{Cr(VI)}} \qquad (4-20)$$

$$\mathrm{Cr(VI)} + \mathrm{Fe(II)} \longrightarrow \mathrm{Cr(III)} + \mathrm{Fe(III)} \qquad (4-21)$$

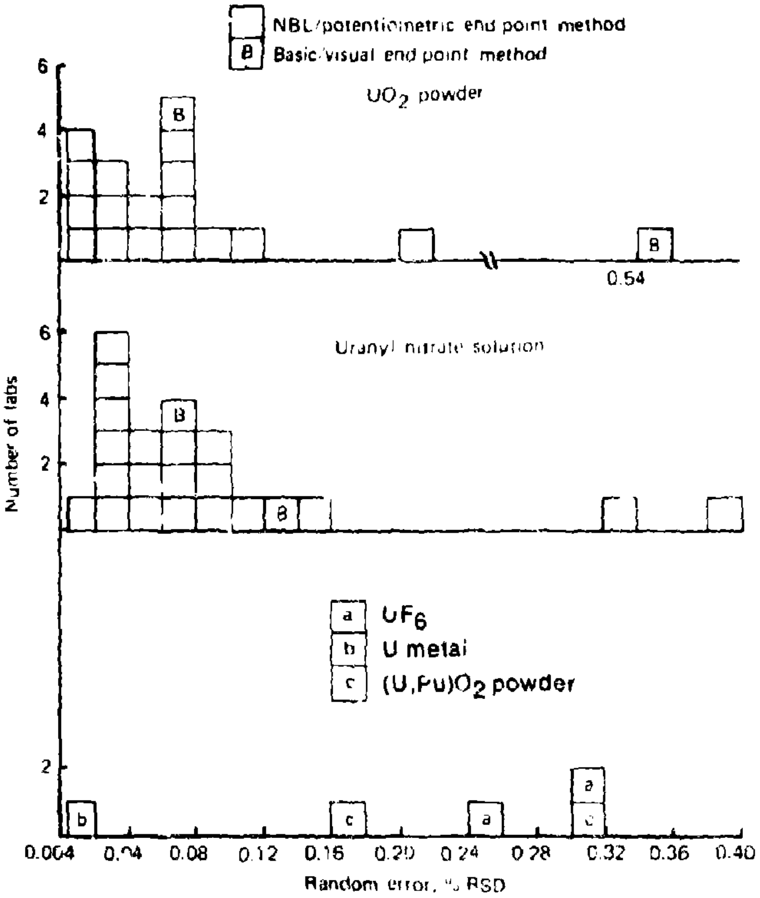

Figure 4.5 Performance of Davies and Gray titrimetric method for uranium—survey of exchange programs.

From the total amount of dichromate used in oxidizing U(IV) to U(VI) (reaction 4–20), as determined by the back-titration of excess dichromate (reaction 4–21), one can calculate the quantity of U in the sample. The total time required for one operator to perform 10 determinations is estimated to be 4 to 6 h. The estimate includes sample weighing, dissolution, and titration.

Lead Reduction/Dichromate Titration Method

This method consists of (1) passing the sample solution through a lead reductor to reduce the U(VI) to U(IV), (2) collecting the reduced solution under excess ferric sulfate, and (3) titrating the iron (II) formed with standard potassium dichromate solution. The chemical reactions involved are

$$\mathrm{U(VI)} \xrightarrow{\mathrm{Pb}} \mathrm{U(IV)} \qquad (4\text{–}22)$$

$$\mathrm{U(IV)} + \underset{\text{excess}}{\mathrm{Fe(III)}} \rightarrow \mathrm{U(VI)} + \mathrm{Fe(II)} + \underset{\text{excess}}{\mathrm{Fe(III)}} \qquad (4\text{–}23)$$

$$\mathrm{Fe(II)} + \mathrm{Cr(VI)} \longrightarrow \mathrm{Fe(III)} + \mathrm{Cr(III)} \qquad (4\text{–}24)$$

From the total amount of Fe(III) used for oxidizing the U(IV) to U(VI) (reaction 4–23), as determined by the back-titration of the Fe(II) produced in reaction 4–23 with dichromate (reaction 4–24), one can calculate the quantity of U in the sample.

Jones Reduction/Ceric Sulfate Titration Method

The method described in Reference 10, p. 181, Reference 4, p. 108, and Reference 69 requires a preliminary separation and/or mercury cathode electrolysis to free the solution of interfering impurities. The U(VI) is reduced in a Jones reductor to a mixture of U(III) and U(IV); the mixture is then air oxidized to bring all the U to the U(IV) oxidation state and titrated to U(VI) with excess standard ceric sulfate solution. The excess ceric ion is back titrated with standard ferrous ammonium sulfate solution to the reappearance of the bright orange color of the ferroin indicator. The advantages of titrations with Ce(IV) over dichromate are a sharp visual end point and a lower indicator blank in the case of ferroin (Ref. 1).

Reviews of a number of methods in which U(VI) is reduced to U(IV) with Jones or lead reductors and then titrated with standard ceric sulfate solution are given in References 1 and 9.

Scope of Applications

Jones Reduction/Dichromate Titration Method

The method as described in References 150, 151, and 174 is recommended for the determination of [illegible] U metal and U compounds of high purity. It is particularly applicable to assay of uranium hexafluoride and for checking the performance of the gravimetric method. The U content of the sample must be known quite closely. Accurate and precise results can be obtained by this method when the sample to be titrated contains 2 to 5 g of U.

Lead Reduction/Dichromate Titration Method

This method has been recommended for determination of U in the form of oxide or metal containing elements such as Mo that are reduced to air-unstable states in the Jones reductor. These elements interfere with the determination of U either by consumption of reagent or by inducing oxidation of U(IV) to U(VI) during the aeration. The lead reductor reduces U(VI) to the U(IV) state only, thereby eliminating the air oxidation of U(III) to U(IV) required when the Jones reductor is used.

Jones Reduction/Ceric Sulfate Titration Method

This method has been applied to U metal and its alloys, UO_2 powder, UNH, and (U,Th) carbide beads.

Summary of Performance

Table 4.19 lists the performance of six redox method variations as applied to several pure material types.

A general description of the three most commonly used methods has been presented in the previous paragraphs. Specific applications of all six method variations are discussed briefly in this section under headings that correspond to the literature, user, and exchange program source categories listed in the table.

Equipment

The apparatus required for the two dichromate titration methods described previously includes standard laboratory equipment, a Jones or lead reductor, a titration cell with indicator and reference electrodes, and a high-impedance-input precision millivolt meter (pH/mV meter). The ceric sulfate titration method requires the standard laboratory equipment, Jones reductor, and a magnetic mercury cathode apparatus to remove metal impurities. A special coating removal apparatus (high-temperature tube furnace and associated glassware and flow control equipment) and an ion exchange column are also needed for U-Th carbide fuel bead material (Ref. 69).

Major Sources of Error

Weighing uncertainty, improper conditioning of the reductor column, inadequate oxidation of U(III) to U(IV) during aeration, and a change in the titer value are all sources of error to be considered in a redox titration. Specific interferences for each method are described in the following paragraphs.

Table 4.19 Summary of performance: alternative redox methods

Method	Application	Performance (% RSD)		Source[a]
		Random Error	Systematic Error	
Jones reduction, excess Cr(VI), back titrate with Fe(II), potentiometric end point	Uranium metal	0.031	—	U
		0.007	—	E
	U_3O_8 powder	0.006	—	L
		0.049	—	U
Jones reduction, titrate with Cr(VI), visual end point, or, back titrate excess Cr(VI) with Fe(II) to potentiometric end point.	UO_2 powder	0.021	—	E
	UNH	0.23, 0.078	—	E
Jones reduction, Ce(IV) titration, ferroin visual end point	Zircaloy-base alloy, 3% to 10% U	0.25	—	L
	U alloy, standard material	0.16	0.049	U
	U alloy, process material	0.43[b]	0.049	U
	UO_2 powder	0.015, 0.70	—	E
	UNH	0.11	—	E
	Uranium solutions	0.09	—	L
	U-Th carbide fuel beads	0.13	—	L
Lead reduction, Fe(III) oxidation, titrate Fe(II) formed with Cr(VI)	U_3O_8	0.03	—	L
Cr(II) reduction, Cr(VI) titration, potentiometric end point	U_3O_8 standard material	0.085	0.033	U
	UNH crystal, 55% U	0.13	0.033	U
Ti(III) reduction, Fe(III) oxidation, titrate Fe(II) formed with Ce(IV), potentiometric end point	Uranium metal	0.002	—	F

[a] E = survey of exchange programs; L = literature survey; U = users' survey of production facilities.

[b] Includes sampling error

Jones Reduction/Dichromate Titration Method

For high-purity materials such as UF_6 or ceramic-grade uranium dioxide, serious interference from impurities is not expected—with the possible exception of Fe. Because Fe interferes with the method, its concentration in the sample must be known. If the Fe concentration is in excess of 100 µg/g, a correction must be made. Most interferences occur as a result of the reduction step (Ref. 9). Ions of metallic impurities that are reduced by Zn amalgam and are oxidized by dichromate interfere. These metals include Fe, Sn, Mo, V, W, and Nb. Some metals such as Ti and Cr are reduced in the reductor but are completely oxidized in the aeration step and, therefore, do not interfere. Samples that contain impurities at levels sufficient to cause interferences must be treated by a suitable extraction or ion-exchange procedure to remove the interfering elements.

Lead Reduction/Dichromate Titration Method

Elements that are reduced by the lead reductor and subsequently oxidized by Fe(III) will interfere. Metals such as Fe, Mo, Ti, W, V, and Nb can be expected to interfere. Sn may interfere. Nitrates, nitrites, and certain organic compounds can interfere, as they do when the reduction is done with Zn amalgam.

Jones Reduction/Ceric Sulfate Titration Method

Tungsten in excess of 100 µg in the portion of the sample to be analyzed can be expected to interfere. In addition, the dissolution and separation procedures used for the U-Th carbide bead material must be followed carefully to avoid loss of U.

Measurement Control Requirements

At least two portions of a working standard traceable to NBS measurements should be analyzed each day, and the results should agree with the established value within 0.05%. This material should represent as nearly as possible the type of samples being analyzed. The procedures being used should be the same for both the test material and the samples.

Data Analysis Requirements

The calculations involved in determining U content for each of the methods are basically the same. The volume of titrant used in milliliters is multiplied by its normality in gram equivalents U per milliliter and divided by the sample weight or aliquot volume. The normality value is based on the atomic weight of uranium corrected for isotopic composition.

Survey of Selected Literature

Jones Reduction/Dichromate Titration Method

This method was shown (Ref. 151) to have a high precision and accuracy on U_3O_8 when essentially pure uranyl fluoride was pyrohydrolyzed and ignited for 200 h. The procedure used a volumetric titration with standard potassium dichromate solution. For seven determinations, the average percentage of U found was 84.819, with a relative standard deviation of 0.006 and a bias (based on an assumed theoretical value of 84.802) of +0.017 ± 0.0046% U at the 95% confidence level.

Lead Reduction/Dichromate Titration Method

This method was applied to U-oxide samples of known impurity content by Byrne, Larsen, and Pflug (Ref. 175). They report results for 29 samples that were fumed with sulfuric acid, evaporated to dryness, and taken up in a mixture of sulfuric and hydrochloric acid. Samples contained up to 2000 μg Mo/g, 1000 μg Fe/g, and 200 μg Si/g. Average recovery was 100.00 ± 0.03%.

Jones Reduction/Ceric Sulfate Titration Method

This method was applied to the determination of 3% to 10% U in zircaloy-base alloys (Ref. 4, p. 108; Ref. 10, p. 181). The summary of the method reads:

> After the sample has been dissolved in hydrofluoric acid, the solution is freed from interfering impurities by mercury cathode electrolysis followed by fuming with sulfuric acid. The U is reduced in a Jones reductor to a mixture of U(III) and U(IV); the mixture is then air oxidized to bring all the uranium to the U(IV) oxidation state and titrated to U(VI) using a standard ceric sulfate solution.

Ferroin was used as the indicator. From the routine use of this method involving "several thousand" samples, a relative standard deviation of 0.25% for a single determination has been obtained.

The method has also been applied to U,Th carbide fuel bead material (Ref. 69). Seven- to 15-gram samples are first treated with Cl_2 at elevated temperature to volatilize the pyrocarbon and silicon carbide coatings. The remaining sample is then dissolved in HNO_3-HF and finally taken up in 6*M* HCl. The Th and U are separated by adsorbing the U on AGl-2X ion exchange resin, which is then stripped by eluting with dilute HCl. The resulting U solution, containing approximately 100 mg U, is electrolyzed by mercury cathode electrolysis to remove interfering impurities, reduced by Jones reduction, oxidized to U(IV) by aeration, and titrated to U(VI) with excess ceric sulfate. The excess ceric sulfate is back titrated with standard ferrous ammonium sulfate to the reappearance of the bright orange color of the ferroin indicator. In repeated analyses of nine samples of beaded fuel particles, the relative standard deviation was 0.13%. Prepared solutions containing known amounts of U were titrated along with the actual bead samples. Analysis of 12 known U solutions, excluding the separation and dissolution steps, gave an average recovery of 99.94% with a relative standard deviation of 0.09%.

Survey of Production Facilities

Jones Reduction/Dichromate Titration Method

This method has been applied to U metal and U_3O_8 powder. The basic procedure described earlier is used. Approximately 5 g of U dissolved in 7.5% H_2SO_4 is reduced with Zn amalgam (Jones) and air oxidized to U(IV). Excess solid $K_2Cr_2O_7$ is added and back titrated with ferrous ammonium sulfate to a potentiometric end point. The random error for the measurement of 168 pure U metal samples over a 2-year period was 0.031% RSD. For U_3O_8 powder, a relative standard deviation of 0.049% was obtained on 45 samples over a 1-year period.

Lead Reduction/Dichromate Titration Method

No routine user data were available for the method.

Jones Reduction/Ceric Sulfate Titration Method

This method has been applied to approximately 8% U in U-alloy materials. The material is dissolved in hydrofluoric acid and pretreated by mercury cathode electrolysis and H_2SO_4 fuming to remove impurities. The sample containing 70 to 90 mg of U is reduced with Zn amalgam (Jones) and air oxidized to U(IV). Excess ceric sulfate is added and back titrated with standard ferrous ammonium sulfate solution to the bright orange color of the ferroin indicator. Replicate measurement on 90 alloy samples over a 1-year period yielded a random error, including sampling errors, of 0.43% RSD. Duplicate measurements on 31 synthetic control standard samples were made during the same time interval, giving a relative standard deviation of 0.16 percent. A measurement systematic error of 0.049% RSD was obtained by statistically combining the standard deviation of the mean for the standard measurements and the total uncertainty of the standards certified value.

Chromous Reduction/Dichromate Titration Method

A sample of UNH crystals containing 150 to 275 mg U is dissolved in water, fumed in H_2SO_4, and reduced under nitrogen atmosphere with chromous sulfate. The sample is air oxidized to U(IV) and titrated under nitrogen to a potentiometric end point with potassium dichromate.

Replicate sample measurements over a 1-year period yielded a random error of 0.13% RSD for pure UNH crystalline material. Replicate measurement of a U_3O_8 standard solution over the same time period yielded a random error of 0.085% RSD. A systematic error of 0.033% RSD was obtained by statistically combining the standard deviation of the mean for the standard measurements and the total uncertainty of the standards certified value.

Survey of Exchange Programs

Jones Reduction/Dichromate Titration Method

Two variations of this method have been used in the SALE program (Ref. 154). The first involves a cupferron extraction to remove impurities; Jones reduction and aeration to convert to the U(IV) oxidation state; and finally, titration with potassium dichromate to a diphenylamine sulfonate visual end point. The second variation also includes the preliminary extraction, reduction, and aeration steps. The U(IV), however, is oxidized to U(VI) with excess solid potassium dichromate, which is back titrated with standard ferrous ammonium sulfate solution to a potentiometric end point. Relative standard deviations of 0.23% and 0.078% were reported by two laboratories for UNH. A relative standard deviation of 0.021% was reported by one of the laboratories for uranium dioxide powder. No distinction was made regarding the method variations used in obtaining these values. The gravimetric/potentiometric end point method, however, should be the more precise.

The gravimetric dichromate addition/potentiometric end point method variation described is used by one of the uranium metal exchange program participants for the assay of U metal. (Personal communication with J. W. Charles, Jr., Oak Ridge Y-12 Plant, Nov. 1980.) A random measurement error of 0.007% RSD is reported for 16 sample measurements over a 2-year period.

Lead Reduction/Dichromate Titration Method

No routine exchange program data are available for this method.

Jones Reduction/Ceric Sulfate Titration Method

Two participants of the SALE program use this method, which employs a mercury-cathode electrolysis step to remove impurities, Jones reduction and aeration to convert to the U(IV) oxidation state, and titration to U(VI) with standard ceric sulfate solution. Relative standard deviations of 0.015% and 0.70% were obtained by two laboratories for UO_2 powder. One of the these laboratories reported a relative standard deviation of 0.11% for UNH.

Ti(III) Reduction/Ceric Sulfate Titration Method

One uranium metal exchange program participant uses this method for the assay of U metal. A sample containing approximately 0.1 g of U is dissolved in a mixture of 1:1 6*N* nitric and sulfuric acid and then diluted to approximately 1*N* acid with distilled water. The nitric acid is destroyed by the addition of sulfonic acid. The U(VI) is reduced to U(IV) by the addition of titanium trichloride. The U(IV) in turn is oxidized by the addition of ferric chloride. The Fe(II) from this reaction is titrated with ceric sulfate to a potential of 800 mV as measured on a potentiometer. Iron will interfere in this titration. A relative standard deviation of 0.002% was obtained for 16 sample measurements over a 2-yr period.

4.7.4 Complexometric Methods

Description of Method

Reagents that form stable complexes can be used in titrimetric analysis if a suitable end point indicator is available. The complexing agent can be used alone, provided it either forms or removes a colored product, thereby providing a self-indicating end point. An end point indicator is used if the complexing agent does not meet the above conditions. The indicator must be a dye that forms a colored complex with a slightly lower stability constant than the compound being titrated.

The disodium salt of (ethylenedinitrilo) tetraacetic acid (EDTA) is probably the most commonly used complexometric titrant for Th and Pu as well as U. Relatively strong complexes are formed, resulting in sharp end points. The propensity of EDTA to form complexes with many elements in the periodic chart constitutes a major problem in the use of this reagent. However, by careful selection of parameters, such as pH and indicator, and by selective complexing or total separation of potential interferences, EDTA titrations can be used for the determination of U.

Complexometric titrations probably offer no advantage over oxidation-reduction methods for determining U and do not provide equivalent precision (Ref. 76). Typically, relative standard deviations of 1% or less may be obtained.

Scope of Applications

The complexometric determination of U is applicable to a variety of samples provided that interfering elements have been removed or selectively complexed. In general, these methods will be applied to relatively pure product solutions. Methods can be based on complex formation with either U(VI) or U(IV). Sample size requirements range from 0.01 to 50 mg of contained U. A method for sequential determination of Th and U has been described in Reference 176.

Summary of Performance

Several complexometric methods for the determination of U in solutions are found in the literature, summarized in Table 4.20, and discussed in more detail in the "Survey of Selected Literature." Method performance, although stated in rather vague terms in some cases, is also presented. No routine user or exchange program data were available.

Table 4.20 Summary of performance: Complexometric determination of uranium

Application	Method	Performance
UO_2^{2+} in uranium solutions	EDTA titration, high-frequency (oscillometer) end point, 9 to 27 mg UO_2^{2+}	0.40 to 0.92 (% relative accuracy)
	EDTA titration, PAN visual end point, pH 4.4 to 4.6, 11 to 100 mg UO_2^{2+}	<0.3 mg (absolute error)
U(IV) in uranium solutions	EDTA titration (by weight), photometric end point (550 nm), pH of 4.4, 0.012 to 9.00 mg U	5.0 to 0.1 (% RSD)
	EDTA titration (by weight), photometric end point (320 nm), pH of 4.0, 1.22 mg U	0.5 (% RSD)
	EDTA titration, thorin visual end point, pH of 1.5, 0.1 to 50 mg U	3 to 0.3 (% relative accuracy)
	EDTA titration, methylthymol blue end point, pH of 3, 25 mg:	
	Photometric end point	0.095
	Visual end point	0.24 (% RSD)
	DTPA titration, xylenol orange visual end point, 47.2 to 953 μg U	1.3 to 0.8 (2σ error, %)
U(IV) in (U,Th)O_2 solutions	Quantitatively mask Th with EDTA, reduce to U (IV) and complex with excess EDTA; back titrate with standard Th solution to xylenol orange visual end point	"Better than 1%" (precision)

DTPA = Diethylenetriamine pentaacetic acid; EDTA = (Ethylenedinitrilo) tetraacetic acid; PAN = 1-(2-pyridylazo)-2-naphthol.

Equipment

The apparatus required for most of the procedures consists of standard analytical laboratory items. A simple spectrophotometer-titration assembly is required for the methods described in References 177 and 178. Complete assemblies for photometric titrations are available from several manufacturers. Some units use flow-through cuvettes that are placed in the sample compartment of the spectrophotometer. In others, fiber optic probes connected to the spectrophotometer dip into the beaker in which the titration is carried out. Costs of complete assemblies run from $1000 to

$10,000. Photometric detection of the end point can be applied to most of the methods under discussion. A high-frequency oscillator is required for the method of Reference 179. Due to the simplicity and relatively low cost of the equipment required, complexometric methods may find application for routine process control carried out at the production line, rather than in the analytical laboratory.

Major Sources of Error

Sources of error in complexometric methods are those typical of titrimetric analysis: pipetting and/or weighing errors, end point detection errors, and inadequate pretreatment. Specific interferences in each method are given in "Survey of Selected Literature." Palei and Karalova (Ref. 180) found that the interference due to fluoride ion can be reduced or eliminated by addition of an excess of beryllium.

Measurement Control Requirements

Aliquots of a standard solution prepared from a primary reference standard such as NBS SRM 950 should be analyzed at least once per shift. Control charts based on the average values should be established. If a measured value exhibits a change at the 0.05 significance level, a replicate measurement should be made. If the second measurement confirms the observed change, the reason(s) for the change should be investigated and a recalibration should be performed. Routine accuracy and precision checks are recommended. The accuracy check can be based on the results of the assay of standard samples. Precision checks should be based on replicate analysis of standard samples made over a period of time (several days to 1 week). Procedure recalibrations should be made whenever reagents are replenished.

Data Analysis Requirements

The calculation of the U concentration is dependent on the particular method being used. A correction for the reagent blank will be required. A typical calculation for a one-to-one complex is as follows:

$$C = \frac{1000\ W(V_2 - V_1)M}{V_a} \qquad (4\text{–}25)$$

where

C = concentration of uranium, μg/mL
W = atomic weight of uranium, g/mole
V_2 = sample titer, mL
V_1 = blank titer, mL
M = molarity of titrant solution, mole/L
V_a = volume of initial sample aliquot, mL

Survey of Selected Literature

Cabell (Ref. 181) studied the complexes of Th and uranyl ions, and Rao and Somidevamma (Ref. 182) reported on their investigation of the uranyl-EDTA complex. It was found that uranyl ion forms a 2:1 complex with EDTA. The uranyl-EDTA complex is the basis of two of the complexometric procedures (Refs. 178, 179 and 183) presented subsequently. The other methods use the complex of U(IV) with EDTA and require reduction of U to U(IV) prior to titration.

Hara and West (Ref. 179) describe a complexometric method using high-frequency (oscillometric) detection of the end point. They found that the trisodium salt of EDTA yielded the sharpest end point. Since EDTA is nonspecific, interferences from other heavy metals were expected. Although Ba, Sr, Ag, Tl(I), and the alkali metals did not interfere directly, they did have an effect, as a result of loading of the oscillator, that was produced by all electrolytes. Acetate and oxalate ions interfered strongly while sulfate ion reduced the sharpness of the end point. Chloride, iodide, bromide, iodate, chlorate, bromate, and nitrate did not interfere other than through the loading effect. Samples containing 9.00 and 27.04 mg of uranyl ion were analyzed with relative accuracies ranging from 0.40% to 0.92%. Insufficient data are given to calculate the precision of the method.

Lassner and Scharf (Ref. 183) developed a method for the determination of uranyl ion, based on titration with EDTA to a visual end point with 1-(2-pyridylazo)-2-naphthol (PAN) as the indicator. The titration is performed in a water-isopropanol solution (1:2) at 80°C to 90°C. The aqueous solution is buffered to a pH of 4.4 to 4.6 with hexamethylenetetramine before addition of the isopropanol. The method was evaluated for sample sizes ranging from 11 to 100 mg. The maximum absolute error was 0.3 mg, which corresponded to the U equivalent of the excess EDTA titrant required to assure complete titration. All ions forming complexes with EDTA at pH 4.5 will interfere. The authors recommend several modifications that will minimize such interferences. However, the resulting procedures are somewhat complicated and separation of the U prior to analysis would be preferable.

Brück and Lauer (Ref. 178) describe a method that is a modification of that developed by Lassner and Scharf (Ref. 183). The sensitivity of the method was increased by using weight titration coupled with spectrophotometric detection of the end point at 550 nm. The titration was performed in isopropanol-water medium at room temperature. The aqueous solution was adjusted to pH 4.4 prior to dilution with isopropanol. The modified method was applied to quantities of U varying from 0.012 to 9.00 mg with relative standard deviations ranging from 5.0% to 0.1%, respectively. Because of the low dissociation constant of the U-PAN complex, it was found that the titer of the EDTA solution could not be used to calculate the U content at the higher concentration levels. The method has a systematic error that varies from zero to about +60 μg of U, depending on the total amount of U. The authors indicate that it is necessary to standardize the EDTA solution with a standard U solution having a concentration close to that of the unknown samples. Interferences are not discussed but should be similar to those reported in Reference 183.

Brück and Lauer also present the results of a limited investigation of the determination of U(VI) using ultraviolet end point detection (320 nm). The method is, otherwise, similar to the PAN end point procedure except that the optimum pH is 4.0 rather than 4.4. The relative standard deviation was 0.5% for 1.22 mg of U.

An EDTA-titration method using thorin as an indicator has been developed by Palei and Hsu (Ref. 184). The optimum pH range is 1.0 to 1.8. Uranium (VI) in perchloric acid is reduced electrolytically on a mercury cathode and diluted to a known volume. An aliquot of the solution is adjusted to pH 1.5 and diluted to 100 mL. The indicator is added and the solution is titrated with EDTA after heating to 30°C. Thorium, bismuth, and zirconium interfere because they form complexes with thorin that are the same color as the uranium-thorin complex. Zirconium also forms a precipitate. Ti(III) and V interfere by destroying the indicator. Ti(IV) and sulfate ions decrease the sharpness of the end point. Cobalt, copper, and mercury interfere strongly with the determination. Divalent tin interferes by producing a precipitate that adsorbs the indicator. Arsenate, molybdate, and tungstate also interfere. Fluoride interference can be eliminated by addition of an aluminum salt. The method is applicable to samples containing 0.1 to 50 mg of U, with errors (relative accuracies) varying from 3% to 0.3%, respectively. No precision data are available.

Keil (Ref. 177) describes a method for determining <25 mg U in 50 mL of solution by EDTA titration of U(IV), using methylthymol blue as the indicator. Ascorbic acid is added to the U solution as buffer and to increase the solubility of U by complex formation. The pH is adjusted to 3 ± 0.25. Solid sodium dithionite ($Na_2S_2O_4$) is used to reduce U to the tetravalent state. The reduction takes about 2 to 3 min. Uranium (IV) is then titrated with EDTA until the end point is almost reached. Potassium periodate (KIO_4) solution is added to prevent precipitation of sulfur due to decomposition of sodium dithionite, and the titration is continued to the end point. Detection of the end point may be visual or spectrophotometric. Keil's paper contains a detailed study of interferences. Some elements interfere by precipitating as sulfides; others catalyze the decomposition of sodium dithionite, leading to precipitation of sulfur. Still other elements decrease the sharpness of the end point. The elements In(III), Pb(II), Sn(II), Th(IV), Sc(III), Y(III), and most lanthanides are titrated along with U. Separation of the U by extraction with triphenylarsinoxide in chloroform from solutions containing EDTA and sodium nitrate is recommended. In the photometric titration of pure U solutions containing 25 mg, a relative standard deviation of 0.095% was achieved. When visual end point detection was used, the relative standard deviation was 0.24%.

The successive complexometric determination of Th and U has been described in somewhat vague terms by de Heer, der Plas, and Hermans (Ref. 176). As best we can determine, the method involves direct titration of Th(IV) with EDTA at pH 3.5 in the presence of U(VI) to an end point, addition of excess EDTA, reduction of U(VI) to U(IV) with sodium dithionite, adjustment of the pH to 3.5 to 4.0 and back titration of the uncomplexed EDTA with standard Th solution. Xylenol orange is used as indicator. The authors recommend the procedure as a routine control method for mixed Th-U oxides. The reference lacks sufficient detail to permit critical evaluation of the method. Precisions of better than 1% are claimed. It is also claimed that arsenazo can be used as the end point indicator.

Rykov, Piskunov, and Timofeev (Ref. 185) describe a method using diethylenetriamine pentaacetic acid (DTPA) as the complexing agent with xylenol orange as the end point indicator. The method is reported to be applicable to the determination of Th(IV), Np(IV), and Pu(IV) as well as U(IV) by proper adjustment of the sample acidity. Fe(III), Hg(II), Zr(IV), Pu(III), and pentavalent and hexavalent actinides interfere with the determination. However, the authors suggest use of the method to determine U(IV) in the presence of U(VI) and Np(IV) in the presence of Np(V). The method is applicable to amounts of U ranging from 0.05 to 50 mg. The 2σ error varied from 1.3% to 0.8% for samples of 47.2 μg and 953 μg, respectively ($0.3M$ HNO_3 solution). No indication of the effects of Th(IV), Np(IV) or Pu(IV) on the U determination is given in the paper. Quantitative interference would be expected.

Survey of Production Facilities

No routine data were available.

Survey of Exchange Programs

This method was not evaluated by these programs.

4.7.5 Controlled-Potential Coulometry

Description of Method

Controlled-potential coulometry (CPC) may be regarded as a special kind of redox titration in which electric current is used as the titrant. In comparison with most redox titrations, coulometry has the advantage of high precision with small amounts of U (2 to 10 mg per determination) and is relatively free from interferences. The technique readily lends itself to remote operations, because only the coulometric cell needs to be in the glove box or hot cell, and the electronics can be outside.

In analysis by CPC, the species to be determined is quantitatively electrolyzed at an electrode whose potential is maintained at such a value that unwanted electrode reactions are precluded. The potential of the working electrode is controlled by means of a potentiostat.

In a normal electrolysis, the current decreases exponentially as the reaction proceeds, until a background current is attained. The electrolysis is then terminated. From the quantity of electricity required by the reaction (measured by means of a current/time integrator), the amount of the substance being determined can be calculated using a form of Faraday's Law:

$$w = \frac{M}{nF} \int_0^t i\,dt \tag{3-26}$$

$$= \frac{MQ}{nF}$$

where

w = weight of U(VI) electrolyzed, g
M = gram-atomic weight of U (adjusted for isotopic composition)
n = number of electrons involved in the overall reaction (in the case of U, $n = 2$)
F = Faraday constant, 96,487 coulombs/mole (based on the relative atomic mass of ^{12}C as 12)
t = time of electrolysis, s
i = electrolysis current, amperes
Q = quantity of electricity, coulombs

The calculation assumes that only one electrochemical reaction (in this case, reduction) occurs with the element being measured. Therefore, conditions must be precisely controlled so that all the current passing through the coulometric cell produces the desired electrochemical reaction; i.e., the current efficiency is 100%. Impurities, including dissolved oxygen and carbonaceous material, that can interfere by being electrolytically oxidized or reduced under the conditions of the coulometric determination must be removed. Detailed discussions of the theory and applications of CPC are available (Refs. 186 through 189).

The amount of U present can also be calculated from calibration of the instrument obtained by the analysis of standard solutions (chemical calibration). For the determination of U, chemical calibration is preferred to electrical calibration (based on Faraday's Law).

The coulometric determination of U is based on the reduction of U(VI) to U(IV). The electrolytic conversion proceeds in two steps. At the electrode surface, U(VI) undergoes a reversible, one-electron reduction to U(V):

$$UO_2^{2+} + e^- \rightarrow UO_2^+ \qquad (4\text{–}27)$$

Then, in the bulk of the solution, U(V) rapidly disproportionates:

$$2UO_2^+ + 4H^+ \rightarrow UO_2^{2+} + U(IV) + 2H_2O \qquad (4\text{–}28)$$

Hence, the result of exhaustive electrolysis is reduction of U(VI) to U(IV), a two-electron change even though the electrode reaction itself involves a single electron. The overall reaction is irreversible.

In the "standard" method for the coulometric determination of U, 0.5*M* sulfuric acid is used as the supporting electrolyte. The reduction of U(VI) proceeds quantitatively when the potential of the Hg pool working electrode is controlled at −0.325 V versus the saturated calomel electrode (SCE). There is no interference from Pu, Fe, and most other impurity elements, provided a preliminary electrolysis at +0.085 V versus the SCE is performed.

Scope of Applications

Controlled-potential coulometry has been applied to a wide variety of U materials, ranging from relatively pure U solutions to various kinds of alloys and irradiated nuclear fuels. Many procedures have been devised to adapt the coulometric technique to new and different types of materials. A listing of some of these is given in Table 4.21. All procedures except one use a Hg pool as the working electrode and require 2 to 10 mg of U per determination. The exception (Ref. 190) uses a Pt working electrode and 200 mg of U per determination.

Controlled-potential coulometry is especially well suited to the analysis of irradiated material, because only a few milligrams are required for a determination. Furthermore, the method lends itself to remote operations, because only the coulometric cell needs to be inside the glovebox or hot cell. The electronics can be outside and some distance away.

Summary of Performance

The "standard" coulometric procedure for determining U, reduction in 0.5*M* H_2SO_4, has proved to be quite accurate, precise, and reliable. A relative accuracy and precision of 0.05% has been obtained (Ref. 189). Interlaboratory studies of the analysis of UO_2 and mixed uranium-plutonium oxides (Refs. 53, 54, 154, and 205) have shown between laboratory agreement of 0.1–0.2% for U assay, including variations due to sample inhomogeneity and errors in sample pretreatment. Table 4.22 summarizes the performance of controlled-potential coulometry as applied to various U materials. Specific applications are discussed in more detail in later paragraphs, which correspond to the literature, user, and exchange program source categories listed in the table.

Equipment

In CPC, the substance determined is electrolyzed at a working electrode, the potential of which is controlled or maintained constant during the electrolysis by means of a potentiostat, and the current is integrated by means of an electronic integrator or coulometer. A typical experimental arrangement for this technique is shown in Figure 4.6. The counter electrode is placed in a separate cell compartment connected to the sample solution through a semipermeable separator to prevent reversal of the desired working-electrode reaction. The solution is stirred vigorously to effect a rapid electrolysis. The time for a normal electrolysis is 15 min.

Instrumentation

Potentiostats, integrators, and digital voltmeters are commercially available from many sources. Some desirable specifications for these instruments follow.

Potentiostat and Integrator

The potentiostat should have an output capability greater than 200 mA and greater than 10 V, an input current of less than 50 nA, and a full-scale currentmeter range of 100 μA or less. The integrator must have a full-scale range of at least 20 coulombs. In terms of a readout of mass of U, the output drift rate should be adjustable to <0.2μg / min and should remain stable within ±0.5 μg per 15 min per month. The electrical calibration of the integrator should remain constant within ±0.1% per year.

Digital Voltmeter

The readout digital voltmeter should be a full four-digit instrument (i.e., capable of indicating 9.999). A 100% overrange is desirable. The accuracy specification should equal or exceed the following: ±(0.02% of reading + 0.01% of full scale) for 6 months at an operating temperature of 25°C ± 5°C.

Table 4.21 Some methods for the determination of uranium by controlled-potential coulometry[a]

Type of Material	Working Electrode	Supporting Electrolyte	Control Potentials (V vs SCE)	Interferences, Comments	Ref.
	Hg	0.5 to 1.0*M* H_2SO_4	+0.085, −0.325	Interferences: Mo(VI), V(V), V(IV), W(VI), Cr(VI), Bi(III), Sb(III), Sb(V), Cu(II), Ti(IV).	191–194 10 (pp. 86-88)
	Hg	1.0*M* potassium citrate, 0.1*M* $Al_2(SO_4)_3$, pH of 4.5	−0.24, −0.64	Tolerance to some interferences higher than in H_2SO_4 medium	191
	Hg	0.5*M* H_2SO_4	−0.34, +0.13	Determination of U and Cu together.	195
Diverse reactor fuel solutions	Hg	0.5*M* H_2SO_4	+0.085, −0.325	Prior extraction with MIBK eliminates most interferences; determination of U after destruction of extractant.	10 (pp. 332-337), 95, 193, 196
Diverse reactor fuel solutions	Hg	0.5*M* H_2SO_4	+0.075, −0.325	Prior extraction with tri-*n*-octylphosphine oxide eliminates most interferences; determination of U in ammonium sulfate back extractant.	104
Solution containing nitrate, nitrite	Hg	0.5*M* H_2SO_4, 0.1*M* sulfamic acid	−0.36	Tolerates up to 4*M* HNO_3.	197
U-Nb alloys	Hg	0.5*M* H_2SO_4, 0.2*M* oxalic acid	+0.075, −0.325	Direct determination for Nb:U <3; tri-*n*-octylphosphine oxide extraction for Nb:U >3.	198
Presence of Mo	Hg	0.06*M* $Na_5P_3O_{10}$, 0.06*M* Na_2SO_4, pH of 7.5 to 9.5	−0.70, −1.40	Interferences: Cr(VI), Cu(II), Ru(IV), nitrate; tolerates Mo:U ≤1:7.	199

Note—See footnote at end of table.

Table 4.21 Some methods for the determination of uranium by controlled-potential coulometry[a] (Cont'd)

Type of Material	Working Electrode	Supporting Electrolyte	Control Potentials (V vs SCE)	Interferences, Comments	Ref.
Presence of Mo	Hg	0.75*M* NaF, pH of 5.5 to 7.0	−0.30, −1.00	Higher tolerance to Fe(III), Al(III), and Mo(VI) than H_2SO_4 method.	200
U-Fe solutions	Hg	0.5*M* H_2SO_4	−0.04, −0.35	Determination of Fe at −0.04 V.	201
U-Pu solutions	Hg	0.5*M* H_2SO_4, 0.2*M* hydrazine sulfate	0.00, −0.39	Prereduction of Pu with hydrazine.	202
U-Pu oxides	Hg	0.5*M* H_2SO_4, 0.2*M* sulfamic acid	+0.055, −0.395	Dissolution HNO_3-H_2SO_4-$(NH_4)_2SO_4$; determination of Pu at +0.055 V.	203
U-Pu solutions	Pt	4.5*M* HCl, 0.5m*M* Bi(III), 0.1*M* sulfamic acid	+0.15, −0.20	Interferences: Mo, Hg, phosphate, fluoride. Bi inhibits H_2 evolution reaction. Pu also determined; sulfuric acid must be added.	190
U-Pu oxides, carbides, and nitrides	Hg	0.5*M* H_2SO_4	+0.085, −0.325	Various dissolution procedures; determination of Pu at Pt electrode. No separation required to 6 atom % burnup.	53, 54
$(U,Pu)O_2$ fuel	Hg	0.5*M* H_2SO_4	+0.075, −0.325	Dissolution in HNO_3-HF.	204

[a] Adapted from Ref. 189.

MIBK = Methylisobutyl ketone; SCE = saturated calomel electrode

Table 4.22 Summary of performance: controlled-potential coulometric determination of uranium

		Performance (% RSD)		
Application	Method	Random Error	Systematic Error	Source[a]
UF_6	Not defined	0.044, 0.46	—	E
UO_2 powder	0.5*M* H_2SO_4 electrolyte, Hg/SCE electrodes, 10 mg U	0.080[b]	0.0[illegible]	U
	H_2SO_4 electrolyte, Hg working electrode, 2 to 20 mg U	0.066	—	E
U metal, standard material	0.5*M* H_2SO_4 electrolyte, Hg/SCE electrodes, 10 mg U	0.15	0.039	U
Uranium nitrate solution, pure	4.5*M* HCl/0.5m*M* Bi(III)/0.1*M* sulfamic acid, Pt gauze electrode, 150 to 300 mg U	0.1 to 0.2	—	L
	H_2SO_4 electrolyte, Hg working electrode, 2 to 20 mg U	0.034, 0.20,	—	E
U-Al_x alloy solutions, irradiated	Extract in MIBK, 0.5*M* H_2SO_4 electrolyte, Hg/SCE electrodes	0.1	—	L
U-Nb alloy solutions	Extract in TOPO (Nb:U > 3), 0.5*M* H_2SO_4/0.2*M* oxalic acid electrolyte, Hg/SCE electrodes	0.2 to 0.5	—	L
Synthetic U-alloy dissolver solutions	Extract in TOPO, back extract into $(NH_4)_2SO_4$, 0.5*M* H_2SO_4 electrolyte, Hg/SCE electrodes	0.1 to 0.2	—	L
Niobium-containing solutions	Direct determination, Hg/SCE electrodes	0.1 to 0.2	—	L
Molybdenum-containing solutions	0.06*M* $Na_5P_3O_{10}$/0.06*M* Na_2SO_4 electrolyte, pH of 7.5 to 9.5, Hg/SCE electrodes, 1 to 5 mg U	0.3 to 0.7	—	L
	0.75*M* NaF electrolyte, pH of 5.5 to 7.0, Hg/SCE electrodes, 6 mg U	<0.5	—	L

Table 4.22 Summary of performance: controlled-potential coulometric determination of uranium (Cont'd)

		Performance (% RSD)		
Application	Method	Random Error	Systematic Error	Source[a]
Uranium solutions	1*M* H_2SO_4 electrolyte, Hg/SCE electrodes, 7.5 to 75 mg U	0.3	—	L
	0.5*M* H_2SO_4 electrolyte, Hg/SCE electrodes:			
	8 mg U	0.1	—	L
	8 μg U	2.3	—	L
	1.0*M* potassium citrate/0.1*M* $Al_2(SO_4)_3$ electrolyte, pH of 4.5, Hg/SCE electrodes, 0.0075 to 0.75 mg U	2.2 to 0.06	—	L
(U,Pu) carbide pellets, 76%	0.5*M* H_2SO_4 electrolyte, Hg/SCE electrodes, 10 mg U	0.17[b]	0.039	U
$(U,Pu)O_2$ powder	H_2SO_4 electrolyte, Hg working electrode, 2 to 20 mg U	0.095	—	E
$(U,Pu)O_2$ pellets	"Standard procedure," Hg/SCE electrodes, U/Pu = 3	0.27	—	L
	H_2SO_4 electrolyte, Hg working electrode, 2 to 20 mg U	0.18	—	E
(U,Pu) oxide, carbide, and nitride solutions	4.5*M* HCl/0.5m*M* Bi(III)/0.1*M* sulfamic acid electrolyte, sequential Pu-U determination, Pt gauze working electrode	0.07 to 0.15	—	L
$UO_2 + PuO_2 + C$, 63% U	0.5*M* H_2SO_4 electrolyte, Hg/SCE electrodes, 10 mg U	0.39[b]	0.039	U

[a] E = survey of exchange programs; L = literature survey; U = users' survey of production facilities

[b] Includes sampling error.

SCE = saturated calomel electrode; MIBK = methyisoutyl ketone; TOPO = tri-n-octylphosphine oxide.

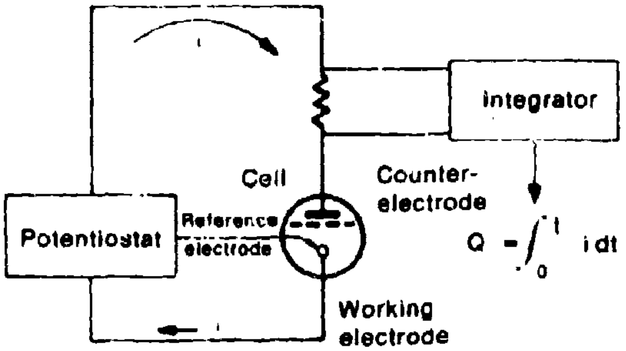

Figure 4.6 Block diagram of apparatus for controlled-potential coulometry (from Ref. 189).

Mercury Pool Cell

The accuracy and precision of CPC are strongly dependent on the design of the electrolysis cell. Some of the design criteria are the speed of electrolysis, speed of solution deoxygenation, uniformity of dc potential distribution at the working electrode, convenience of use, and reliability.

The mercury pool cell shown in Figure 4.7 was designed by Harrar (Ref. 206) and has been widely used with excellent results. Details for the cell construction, assembly, and operation may be found in Reference 207. A somewhat different cell design is described in Ref. 54.

Major Sources of Error

Errors most commonly encountered result from:

(1) Uncertainty in the value of the standard used for instrument calibration
(2) Accuracy uncertainty of the analytical balance
(3) Inadequate removal of oxygen from the cell before and during the electrochemical steps
(4) Malfunctioning reference electrode causing a shift in the actual control potential
(5) Inadequate operator techniques

Interferences in the "standard" method are caused by ions that are electroactive at the reduction potential used or by species that prevent the complete reduction of the U. Interference by many impurity elements more easily reducible than U(VI) is prevented by a preliminary reduction at +0.085 V versus SCE. For example, the interference from Fe(III), Pu(VI), Pu(IV), Cr(VI), Ce(IV), and other strong oxidants is eliminated by the preelectrolysis. Plutonium does not interfere when the Pu/U ratio is 3 or less. Large amounts of electroactive elements that reduce at potentials more negative than −0.325 V versus SCE, such as Cd(II), Zn(II), or Ni(II), can be tolerated. Also permitted, without ill effect, are large amounts of nonelectroactive ions including the alkaline earths, alkali metals, Al(III), Th(IV), and others.

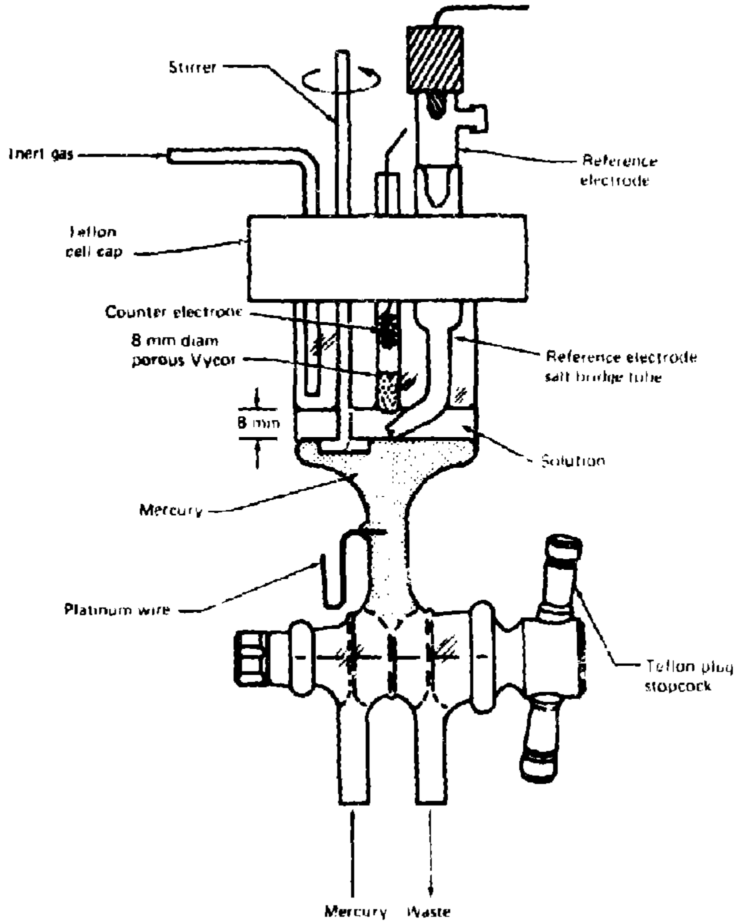

Figure 4.7 Mercury pool cell for controlled-potential coulometry.

Copper(II) is reduced simultaneously with U(VI) and ordinarily would constitute an interference. However, at a Hg electrode in sulfuric acid electrolyte, the reduction of Cu is reversible and that of U is not. The Cu can be quantitatively reoxidized (Ref. 195) in the presence of U(IV), thus providing a correction for its presence.

Molybdenum(VI) interferes at all concentrations and should be removed or kept below 0.05% of the U. Tungsten does not interfere at concentrations up to 0.2%.

Anionic interferences are minimal. Sulfate concentration in the supporting electrolyte can vary within the range from 0.25 to 2.5*M* without effect on the analytical result. The supporting electrolyte may be as high as 5*M* in nitrate, provided enough sulfamic acid or urea is added to destroy any nitrite that may be present. In the presence of nitrate, multivalent trace impurities such as Mo(VI), V(IV), V(V), Ti(IV), Nb(V), and W(VI) can cause interference because of catalytic reduction of nitrate at the electrode surface.

Perchlorate does not interfere. Chloride will interfere seriously in the preliminary electrolysis through the formation of mercurous chloride, but in the reduction of U(VI) chloride can be tolerated at concentrations of up to 0.01*M*. Because of the interferences of nitrate and chloride, it is recommended that samples be fumed with sulfuric acid before electrolysis.

Oxygen interferes seriously with the electrolysis. It is mandatory that the sample solution be purged of oxygen prior to the electrolysis and that an inert gas blanket be maintained within the cell throughout the electrolysis.

Measurement Control Requirements

Chemical calibration of the instrument is preferred to electrical calibration, because the latter can introduce a bias in the determination of U. The standard solution used for calibration should closely resemble the samples to be analyzed.

Instructions for chemical calibration and determination of the background current may be found in References 204 and 207. The chemical calibration factor and the background correction should be verified daily or at the beginning of each shift.

Data Analysis Requirements

Calculate the U content of the sample as follows:

$$U = \frac{(S - B)F_c}{X} \tag{4-29}$$

where

U = grams of U per gram of sample
S = integrator readout voltage for electrolysis of sample aliquot

B = integrator readout voltage for background electrolysis
F_c = chemical calibration factor, grams of U per volt of readout
X = mass of sample aliquot, g

The chemical calibration factor is calculated as follows:

$$F_c = \frac{E_u}{D-B} \; \frac{\text{atomic weight of U}}{2} \qquad (4\text{–}30)$$

where the atomic weight of U has been corrected for isotopic composition and where

E_u = equivalents of U in aliquot of standard solution
D = integrator readout voltage for electrolysis of standard
B = integrator readout voltage for background electrolysis

Survey of Selected Literature

First, some of the results obtained in tests of the "standard procedure" will be discussed. Next, some variants of the "standard procedure" in which preliminary separations are performed are examined. Finally, some procedures that use supporting electrolytes other than sulfuric acid will be considered.

Booman et al. (Ref. 191) determined U in 1*M* sulfuric acid. Amounts of 7.5 to 75.0 mg could be determined with an electrolysis time of 5 to 10 min and a precision of 0.3% RSD.

Jones, Shults, and Dale (Ref. 192) determi[illegible] the 8–mg level in 0.5*M* H_2SO_4. The precision was 0.1% RSD, and recoveries ranged from 99.9% to 100.4% of the amount taken. At the [illegible]-μg level, the precision was 2.3% RSD and the recovery 98.8%.

For the direct determination in the presence of Nb, Shults and Dunlap (Ref. 198) report an RSD of 0.1% to 0.2% and a recovery of 100.2% to 100.7%.

Detailed results of interlaboratory studies of the coulometric determination of U and Pu in ceramic U-Pu materials are given in References 53 and 208. MOX fuel pellets were analyzed. To summarize the results: the relative standard deviations obtained by a single laboratory were 0.07% for Pu and 0.18% for U in MOX sintered pellets having a U/Pu ratio of 3.

The pooled RSDs obtained in the analysis of five samples, four aliquots each, by six laboratories were 0.15% for Pu and 0.27% for U. The RSDs for the calibration titrations were 0.04% for Pu and 0.08% for U.

Shults and Dunlap (Ref. 104) have used TOPO in cyclohexane for extraction of U from a wide variety of U alloy solutions in 1*M* HNO_3. Uranium is back extracted into 3.5*M* ammonium sulfate solution (pH: 2). Recoveries in the determination of U in synthetic dissolver solutions ranged from 99.7% to 100.2%, with a mean of 99.9%. The precision was 0.1% to 0.2% RSD. Analysis of samples with high molybdenum content (Mo:U >1:10) requires preliminary removal of Mo by extraction with α-benzoinoxime.

In the analysis of U-Nb alloys with prior separation (Ref. 198), recoveries of 99.3% to 99.8% and precisions of 0.2% to 0.5% were obtained.

Uranium has also been separated from the products of its nuclear cycle by extraction with methyl isobutyl ketone (hexone) from an acid-deficient aluminum nitrate salting solution (Refs. 10, 95, 193, and 196). The organic matter is then destroyed by evaporation and wet oxidation with sodium bisulfate and perchloric acid prior to coulometric determination of U. Reference 193 reports that the estimated precision of a single laboratory in an interlaboratory comparison with five participating laboratories was 1% RSD. In each case four selected samples were analyzed by two experienced analysts in 2 days. The relative standard deviation between laboratories was 1.6%. Reference 10 states that a 0.3% RSD was obtained for a single determination, based on the analyses by three laboratories of a standard U solution containing 8 mg U/mL. A bias of + 0.3% ± 0.3% was obtained. For routine analysis of duplicate aliquots of irradiated U-Al alloys in one laboratory an RSD of 0.1% was obtained in the analysis of 400 samples.

Booman, Holbrook, and Rein (Ref. 191) propose reduction of U in a 1*M* potassium citrate, 0.1*M* aluminum sulfate medium (pH 4.5). A prereduction is performed to prevent interference from impurities (Cu, Fe, and Ce). For samples containing 0.75 to 0.0075 mg U, the relative standard deviation ranges from 0.06% to 2.2%.

For the determination of U in the presence of Mo, one procedure (Ref. 199) uses a medium of 0.06*M* sodium tripolyphosphate and 0.06*M* sodium sulfate at pH of 7.5 to 9.5. Interfering impurities are Cr(VI), Cu(II), Ru(IV), and nitrate. In an alkaline complexing medium, U(IV) is kept in solution as the result of complex formation, while molybdate ions are not electrically active and do not interfere with the reduction of U, provided the Mo:U mass ratio does not exceed 1:7. For 1 to 5 mg amounts of U, the RSD is 0.3% to 0.7%.

Another procedure (Ref. 200) for the determination of U in the presence of Mo uses a medium of 0.75*M* sodium fluoride (pH 5.5 to 7.0). At the 6-mg level, the recoveries are 100.2% to 100.3% and the precision is better than 0.5% RSD.

Several procedures have been devised for determining U in the presence of Pu. No systematic study has been made of the tolerance of the H_2SO_4 method to Pu, which, as Pu(IV), oxidizes the Hg and is prereduced at + 0.085 V versus SCE. However, the analyses of Pu-U mixtures that have been performed (Ref. 53, 203) show that Pu:U ratios of at least 4 are tolerable. Larger amounts may be permissible if the plutonium is chemically reduced, for example, with hydrazine (Ref. 202).

Davies, Gray, and McLeod (Ref. 190) have determined U in 4.5*M* HCl at a Pt-gauze working electrode. A small amount of bismuth is added to prevent hydrogen evolution and electrode poisoning. Sulfamic acid is added if nitrate is present. Samples containing 150 to 300 mg of U(VI) are required. Molybdenum, mercury, phosphate, and fluoride interfere. The precision of a single determination was found to be 0.1% to 0.2% RSD, and the bias was less than 0.1% when electrical calibration of the coulometer was employed. The method was used for the analysis of pure uranium nitrate solutions.

Kuperman et al. (Ref. 209) use the 4.5*M* HCl plus $5 \times 10^{-4} M$ Bi(III) medium suggested by Davies, Gray, and McLeod (Ref. 190) for sequential determination of Pu and U. In preparing the solution for analysis, all the Pu is oxidized to Pu(VI) by boiling with perchloric acid. Malonic and formic acids are then added for the selective reduction of Cr(VI), Mn(VII, IV, III), and perchloric acid decomposition products. After deaeration of the solution with argon, Pu is coulometrically reduced to Pu(III) at +0.26 V versus SCE for 15 min. The electrode and solution are prepared for the reduction of U by a preelectrolysis at + 0.15 V. Finally, U is reduced at −0.2 V. The precision obtained for the analysis of mixed fuels (oxides, carbides, and nitrides) was 0.02% to 0.07% RSD for Pu and 0.07% to 0.15% RSD for U.

Survey of Production Facilities

The controlled-potential coulometric method for determining U was not used routinely in accountability or process control applications. The Davies and Gray titrimetric and gravimetric methods were found to be more reliable than CPC in most routine applications. In addition, equipment and instrumentation costs and operator qualification requirements were greater for the CPC method.

One method has been used, however, for the determination of U in U metal, UO_2 powder, and Pu-U mixed carbide materials. A 10-mg sample in 0.5 *M*-H_2SO_4 supporting electrolyte is electrolyzed at a Hg pool electrode controlled at −0.325 V versus SCE. A preliminary reduction is made at + 0.085 V to eliminate interference from Pu and most other inpurity elements.

The random error of the method for each material type in percent relative standard deviation is as follows:

Material	*Random Error (% RSD)*
U metal (standard material)	0.15
UO_2 powder	0.080 (includes bulk sampling error)
(U,Pu) carbide pellets, 76% U	0.17 (includes bulk sampling error)
UO_2 + PuO_2 + C, 63% U	0.39 (includes bulk sampling error)

Method performance is verified by measuring a sample of NBS 960 U metal at least twice per week.

The method systematic error, 0.039% RSD, was determined by statistically combining the standard deviation of the mean determined from the replicate verification standard measurements and the total uncertainty of that standards certified value.

Survey of Exchange Programs

Some SALE program participants use CPC to determine U in UO_2 powder, UNH, and U-Pu mixed oxide powder and pellets (Ref. 154). Two to 20 mg of U in a sulfuric acid supporting electrolyte is reduced at a Hg pool cathode under an inert atmosphere. The random measurement error in percent relative standard deviation is reported to be:

Material	*Random Error (% RSD)*
UO_2 powder	0.057, 0.074
UNH solution	0.20, 0.034
$(U,Pu)O_2$ powder	0.095
$(U,Pu)O_2$ pellet	0.18

Two GAE program participants use CPC to determine U in UF_6 (Ref. 155). The UF_6 is hydrolyzed, fumed and dissolved, and a weighed aliquot is taken for analysis by CPC. No specific details of the analysis procedure were available. Measurement random errors of 0.044% and 0.46% RSD were reported.

4.7.6 Spectrophotometry

Description of Method

The spectrophotometric determination of U is based on the absorption of light of a specific wavelength by U compounds or complexes in solution. The fraction of incident light that is absorbed is proportional to the concentration of the absorbing species. The relationship is written as follows:

$$\log \frac{I_0}{I} = abc = A \qquad (4\text{-}31)$$

where

I_0 = intensity of the incident radiation
I = intensity of the transmitted radiation
a = absorptivity

b = path length
c = concentration of the substance
A = the absorbance (sometimes referred to as optical density or extinction)

The molar absorptivity (sometimes referred to as molar extinction coefficient) is a product of the absorptivity a and the molecular weight of the substance.

Beer's Law states that the absorptivity of a substance is constant with respect to changes in concentration. The measured absorbance will thus vary linearly with concentration. However, deviations from this relationship may occur at high concentrations or as a result of competing reactions.

Aqueous acid solutions of U usually contain U in the hexavalent form. The absorption spectrum of U(VI) in the visible region consists of a band with four principal maxima occurring at 426, 416, 403, and 359 nm. Several direct spectrophotometric methods have been developed for the determination of high concentrations of U using one or more of these wavelengths. Measurements have been made at either 416 or 426 nm or both. The wavelengths and molar absorptivities of the absorption bands depend on the solvent and its concentration, the temperature, and complex formation. In 0.5 to 5*M* nitric acid medium, for instance, the absorbance of U is due to UO_2^{2+} and $UO_2NO_3^+$ and is strongly affected by the nitric acid concentration (Refs. 210 and 211). In less than 0.5*M* nitric acid medium, the uranyl absorbance is primarily due to the absorption of UO_2^{2+} and uranyl dimer. In this case the nitric acid concentration is not critical. For determination of U by direct spectrophotometry, the temperature and acid concentration must be reproducibly controlled. To give an idea of the magnitude of temperature effects: an increase of 1 °C in the solution temperature can result in an overestimation of the U concentration by 0.2g/L.

There are a number of chromogens that react with U to form colored complexes. These complexes generally have high molar absorptivities and are suitable for the determination of low concentrations of U. Since Th, Pu, and many other cations may form colored complexes with the chromogens that react with U, a separation is normally required.

Several authors have reviewed the large number of spectrophotometric procedures for the determination of U (Refs. 71, 76, 212 and 213). The procedures that currently have the widest use are those using the following chromogens: dibenzoylmethane, arsenazo-III, tetrapropylammonium nitrate, 4-(2-pyridylazo) resorcinol (PAR), or PAN. These procedures will be emphasized in the discussion of spectrophotometric methods for low concentrations of U.

Scope of Applications

Spectrophotometric procedures may be applied to the determination of U in a variety of materials such as dissolver solutions, waste solutions, and product streams. Spectrophotometric methods have also been applied to the determination of the U content of U metal and U oxide, after dissolution of the solid.

Direct spectrophotometric methods are usually applied to the determination of larger concentrations of U in solution or to samples in which U is a major constituent. Methods covering the concentration range from 20 to 200 g/L have been developed. The precision of direct methods is generally poorer than 0.5% RSD, often 1% to 2%. Differential spectrophotometric methods (Ref. 214) were developed to improve the precision so that the RSD of the measurements would decrease to a level of 0.1% to 0.5% or less. The increased precision is achieved by an appropriate expansion of the scale used for the measurement of light intensities. Scale expansion can be made by placing cuvettes containing solutions of suitable concentrations in the cell compartment of the instrument, and adjusting the transmission (or absorbance) scale with them. In the "transmittance ratio method," the unknown solution is compared with a known solution of slightly lower concentration. In the "ultimate precision method," two reference solutions are needed; one is more concentrated than the unknown solution, the other is less concentrated. Differential spectrophotometry can yield an accuracy and precision comparable to those obtained with titrimetric methods (Ref. 215).

The direct determination of U in nitric acid solution has been used for inline process control of solutions containing high concentrations of U (Refs. 210 and 216). By measuring the absorbance at both 416 and 426 nm, it was possible to apply a correction for variations in the nitric acid contents (Ref. 211). For 0.5 to 5*M* nitric acid solutions, the calculated RSD of the U concentration was 5.4%. For 0.02 to 0.5*M* nitric acid solutions the calculated RSD of the U concentration was approximately 3%. This precision is not adequate for accountability or safeguards purposes but is quite satisfactory for process control. Browning of the optical components may be a problem with process streams containing fission products.

Chromogenic methods are used for the determination of microgram or milligram quantities of U. Relative standard deviations generally fall in the 0.3% to 10% range. The tetrapropylammonium nitrate method (Ref. 95) can be used for sequential determination of U and Pu (Ref. 122). The method has been automated (Ref. 217). A method using benzoyltrifluoroacetone (Ref. 218) is being adapted for the automated system to provide improved U sensitivity. (J.E. Rein, Los Alamos National Laboratory personal communication, July 1979.)

Summary of Performance

Table 4.23 lists the performance of several spectrophotometric methods for determining U in a variety of relatively low-level process or waste solutions. A more detailed discussion of each method will be found later in this section. These discussions will correspond to the literature and user source categories in the table

Equipment

Direct or differential methods require a high-precision recording spectrophotometer with variable slit widths and temperature-controlled sample chamber. A dual beam instrument is preferred for differential methods. The band-pass should be 1 nm or less. Digital readout is desirable. Wavelength accuracy should be within 0.3 nm, and wavelength reproducibility within 0.1 nm. Photometric accuracy and reproducibility should be 0.15% between 1 and 2 absorbancy units. The wavelength range required will depend on the analyses to be performed with the instrument.

For many chromogenic methods (but not the tetrapropylammonium method), a nonrecording spectrophotometer with 10 nm (or less) band-pass is adequate. Digital readout rather than meter readout is desirable. A single beam instrument that covers the 325- to 925-nm wavelength range will cost about $3000.

Major Sources of Error

Sources of error in spectrophotometric methods include volumetric errors, such as in pipetting, dilution, or making solutions up to a specified volume; incomplete separation of U; presence of other oxidation states besides the one desired; failure to set the spectrophotometer to the absorption band maximum; and differences in composition between standards and samples. Temperature control to 0.2°C is required for direct and differential spectrophotometry. Interferences encountered in specific methods are listed in the "Survey of Selected Literature."

Measurement Control Requirements

An aliquot of a standard solution, prepared from a primary standard such as NBS 950, should be analyzed at least once each shift. A control chart based on the average value should be established. Changes in the measured value at the 0.05 significance level require investigation of the reasons for the change before samples are analyzed. A second aliquot should be analyzed to rule out operator error as a cause of the change. If a second analysis confirms the results of the first, a complete recalibration should be done. Any changes in analysis conditions also make recalibration mandatory.

Table 4.23 Summary of performance: spectrophotometric determination of uranium

Application	Method	Performance (% RSD) Random Error	Systematic Error	Source[a]
Uranium solutions	Differential, U(VI), 20 to 60 mg U/mL	0.04, 0.3	—	I
	Uranyl carbonate complex, 0.1 to 10 mg U/mL	"Better than 1%"		I
Process stream	Direct, U(VI), continuous in-line:			
	416 nm	15 to 30 (% error)		I
	416 and 426 nm	< 5 (% error)		I
Carbonate solutions	.3-Dihydroxynaphthalene-6-sulfonic acid complex, continuous flow monitor, 8 to 60 μg U/mL	9.9 to 1.1	—	L
Liquid discharge solutions	Dibenzoylmethane complex, 0.2 to 50 μg/mL	76[b]	0.51	U
ADU filtrate solutions	Peroxide complex, 68 μg U/mL	4.0[b]	—	U
Standard solutions	Tetrapropylammonium uranyl trinitrate complex, 1 to 30 mg U	5 to 2.2	—	L
	Dibenzoylmethane complex	0.6	—	U
		2	0.51	U
	Peroxide complex	0.4	—	U
Purex waste solutions	Arsenazo-III complex after TBP extraction, 1 to 10 μg U	20 to 2	—	L
Purex process solutions	Thenoyltrifluoracetone complex, 0.2 to 1.4 mg U/mL	2	—	L

Note—See footnote at end of table

Table 4.23 Summary of performance: spectrophotometric determination of uranium (Cont'd)

Application	Method	Performance (% RSD)		Source[a]
		Random Error	Systematic Error	
Purex process solutions	Thoria complex, 25 to 250 μg U	2	—	L
Miscellaneous solutions	Dibenzoylmethane complex, 1 to 750 μg U	25 to 0.57	—	L
	Arsenazo-III complex, 1 to 200 μg U	10 to 0.36	—	L
	Tetrapropylammonium uranyl trinitrate complex, automated, 452.5 and 460 nm, 0.12 to 10 mg U	10.4 to 0.2	—	L
	Benzoyltrifluoroacetone complex, 384 and 400 nm, 5 to 80 μg U	2.9 to 0.2	—	L
	4-(2-Pyridylazo) resorcinol complex, >30 μg U	1	—	L

[a] L = literature survey; U = users' survey of production facilities

[b] Sampling error included.

TBP = tributyl phosphate

The precision of the method should be checked routinely by performing replicate analyses (at least five determinations) of known solutions. It is recommended that standard solutions having concentrations at the low, middle, and high end of the range of the method be analyzed.

Data Analysis Requirements

In one method of calculating the U content of a sample, a series of standard solutions of known U concentration is used to obtain an average calibration factor (concentration of U per absorbance unit). The measured absorbance of the sample (corrected for blank and background), the calibration factor, and the volume of the sample are used to calculate the quantity of U in the sample. Alternatively, a calibration equation can be obtained by a least-squares fit of the calibration data. The U concentration in the samples can be calculated with the derived equation.

Survey of Selected Literature

Direct and Differential Spectrophotometry

The direct and differential methods employ a characteristic absorption band of U(VI), either the band at 416 nm or at 426 nm, or both. The procedures designed to be performed in the laboratory are quite simple. They are essentially limited to pure U solutions. They involve dissolution of solid samples (e.g., U_3O_8 or U metal) with nitric acid. The solution is converted to standard conditions of acidity by evaporation to fumes of sulfuric acid or perchloric acid. The residue is dissolved in water, transferred to a volumetric flask, and made up to volume with water. The temperature of the solution is adjusted, and the absorbance is read with the spectrophotometer. The reference solution is either water (in direct spectrophotometry) or a solution of known U concentration, slightly lower than that of the unknown solution (differential spectrophotometry).

Silverman and Moudy (Ref. 219) worked with 10- to 70-mg/mL of U in perchloric acid solutions. They found no interference from Al, Cd, Pb, Fe, Th, or Zr. Comparison of the spectrophotometric results with results obtained by other techniques showed good agreement.

Steele (Ref. 220) also used perchloric acid solutions and found that Cr, Fe, V, Ni, Co, sulfate, and phosphate interfere to a marked degree. In the differential analysis of synthetic solutions, differences between the quantity of U added and the quantity found did not exceed ±0.1%, relative.

Susano, Menis, and Talbott (Ref. 221) performed differential spectrophotometry on uranyl sulfate solutions. The optimum range was 20 to 60 mg of U/mL. The average difference between U present and U found was 0.3% relative, and the precision was within 0.3% RSD.

Thiemann, Kiesslin, and Jansen (Ref. 222) based their method on formation of the uranyl carbonate complex. They pointed out that this complex is the only colored and soluble metal carbonate complex. The U solution is evaporated several times with nitric acid. Addition of an excess of sodium carbonate or potassium carbonate precipitates interfering metal ions. After filtration of the solution, the absorbance of the uranyl carbonate complex is measured at 448 nm. It is claimed that quantities of U between 10 and 1000 mg/100 mL can be determined "to better than 1%." Cuvettes of 0.5- to 5-cm light path are used to cover the concentration range.

Bacon and Milner (Ref. 215) described a procedure for the determination of the U content of relatively pure samples of U_3O_8 and U metal. The sample was dissolved with nitric acid, and the solution was then fumed with sulfuric acid. Solutions that were 4*M* in sulfuric acid were found to give optimum results in differential spectrophotometry at 430 nm. A precision of 0.04% RSD was claimed for solutions containing 28 to 52 g U/L.

Bhargava et al. (Ref 223) investigated the determination of U in aqueous nitric acid solutions and in organic solutions (30% TBP in Shellsol-T). The solutions were found to obey Beer's law up to 30 g/L of U. For higher concentrations of U, differential spectrophotometry was used.

Direct spectrophotometry at 416 nm has been used for the continuous in-line determination of U in process streams. Several instruments have been constructed and tested (Refs. 210 and 216); however, errors as large as 15% to 30% have been encountered with these instruments, because of variations in nitric acid concentration and temperature. Bostick (Ref. 211) has recently shown that by making measurements at both 416 and 426 nm, the U concentration can be determined to within 5% in the presence of varying concentrations of nitric acid and free nitrate ion.

Dibenzoylmethane

This method (Refs. 95 and 224) is based on measurement of the absorbance of the uranium-dibenzoylmethane complex at 415 nm. All of the U in the sample is first oxidized to U(VI) by potassium permanganate. Uranium is quantitatively extracted into methyl isobutyl ketone (hexone) from an acid-deficient salting solution of aluminum nitrate and tetrapropylammonium nitrate. Scrubbing the organic phase with an acid-deficient solution of aluminum nitrate containing tartrate, oxalate, EDTA, and ferrous sulfamate removes most interfering ions.

If large amounts of Th or Ce(IV) are present, the tetrapropylammonium nitrate is eliminated from the aluminum nitrate salting solution and the scrub is performed with the solution of ammonium and sodium diethyldithiocarbamate. A second scrubbing with a solution of mercuric nitrate and aluminum nitrate removes the diethyldithiocarbamate, which otherwise would interfere with the subsequent color formation. The Th elimination procedure does not remove Pu.

Color development takes place in the hexone phase by the addition of dibenzoylmethane in an ethyl alcohol/pyridine mixture. The absorbance is measured and the concentration of the U in the sample is determined either from two comparison standards run at the same time that bracket the unknown, or from a standard curve.

Large amounts of all diverse ions were tolerated except tungstate, ferrocyanide, thiocyanate, and dichromate. No cations interfered and anions usually considered to complex U, such as fluoride, sulfate, phosphate, chloride, and oxalate, were without effect.

Best results are obtained when the sample aliquot contains 30 to 75 μg of U. Solutions containing 30 to 750 μg U/mL may be analyzed. At concentrations above 750 μg/mL, dilutions must be made.

Maeck et al. (Ref. 95) obtained the following precision data for the method:

U determined (μg)	*RSD (%)*
75	0.57
25	0.71
5	3.2
1	25

An interlaboratory evaluation (Ref. 224) of the method by nine laboratories gave an estimated precision of 1.7% RSD for a single determination of samples containing 30 to 750 μg U. This value was obtained by the analysis of four samples in duplicate by two analysts at each laboratory over a period of several days.

Arsenazo-III

This chromogen reacts with either U(IV) or U(VI) to form blue complexes. Spectrophotometric methods have been based on both reactions (Refs. 101, 225, and 226). The reaction with U(IV) is more sensitive; however, the necessity for reducing U(VI) to U(IV) and preventing it from being reoxidized makes procedures based on reaction with U(VI) preferable. Only those procedures are considered here.

Arsenazo-III reacts with a large number of metals and becomes useful only when the selectivity is improved by pH control and the addition of masking agents (Ref. 227). Fritz and Johnson-Richard (Ref. 101) found EDTA to be a versatile masking agent except in the presence of Th, when U was separated by extraction with diethyldithiocarbamate. The amount of EDTA must be controlled because too large an excess interferes with the U color development. Henicksman and Hues (Ref. 228) recommend adding a weighed quantity of EDTA and carefully measuring the volume of arsenazo-III reagent solution added.

In the recommended procedure (Ref. 228), an aliquot of the solution containing 20 to 200 μg of U is taken. If the U is not known to be in the hexavalent state, bromine water is added. The acidity is adjusted with ammonium hydroxide. A triethanolamine buffer solution containing EDTA is added. A carefully measured volume of arsenazo-III solution is added, and the sample solution is diluted to volume. After a 10-min wait for color development, the absorbance is measured at 600 nm versus a reagent blank. The precision for samples containing 20 to 200 μg U was 0.36% RSD. The average recovery for standard U solutions was 100.0%, and for solutions containing tungsten or molydenum, 99.95%. The range of the method can be extended downward by simple changes to measure 5 μg with a 2% RSD and 1 μg with 10% RSD.

Several elements were observed to slow the color development. Large amounts of Mo and W inhibit complex formation. Two hours are required for full color development. Only 5 μg of Nb can be tolerated. If larger quantities are present, several days may be required for full color formation. This time can be reduced to 1 h by adding tartaric acid, increasing the amount of arsenazo-III added, and heating the solution to the temperature of boiling water.

Baumann has reported a procedure for determining U in aqueous Purex waste solutions (Ref. 229). Uranium is separated from fission products by extraction into TBP-xylene. The organic phase is successively scrubbed with ammonium nitrate solution containing EDTA. Uranium is back-extracted with a phthalate buffer solution (pH 2.5) containing the arsenazo-III reagent. The absorbance was measured at 652 nm. Recoveries of 66% to 67% were found by spiking the samples with known amounts of ^{233}U. The standard deviation for the measurement of 1 to 10 μg U was 0.2 μg. Uranium standards were analyzed in the presence and absence of a simulated "fission product mixture."

Tetrapropylammonium Nitrate

In this method, the absorbance of an ion association complex of tetrapropylammonium uranyl trinitrate is measured at 452 nm. The method (Ref. 95) has been applied to a wide variety of aqueous and organic solutions and has been automated (Ref. 217).

Because both U(VI) and Pu(VI) form colored complexes that absorb at different wavelengths, the method can be used for the determination of both elements (Ref. 122). Details will be found under spectrophotometric methods for plutonium (see section 4.9.5).

In the manual method of Maeck et al. (Ref. 95), a sample of 0.5 mL or less, containing 0.5 to 12 mg U, is diluted with an acid-deficient aluminum nitrate/ammonium hydroxide salting solution containing tetrapropylammonium nitrate. The complex is extracted into methyl isobutyl ketone. The absorbance of the organic phase is measured at 452 nm against a reagent blank. No other ions extract and absorb at this wavelength. Cerium (IV) and Th, which are complexed by tetrapropylammonium nitrate, thereby using up the reagent, are the only interferences reported. Because the absorption band is sharp, a high-resolution spectrophotometer or filter instrument employing narrow bandwidth filters is required.

Detailed analytical procedures for the analysis of aqueous and organic solutions (including hot process solutions) are given by Rodden (Ref. 230). Because calibration standards are prepared with natural U, a correction must be applied for enriched U samples. The factor for this correction is the ratio of the average atomic weight of U in the sample to the average atomic weight of natural U. (See Ref. 10, p. 352.) The reliability of the method was determined through replicate analyses of standard aqueous solutions prepared from NBS U_3O_8. The observed precisions were 5%, 2.5%, and 2.2% RSD for single determinations at the 1-, 15-, and 30-mg levels. For best precision, work should be done at U levels above 10 mg.

An automated spectrophotometer (Ref. 217) with narrow band-pass interference filters was constructed at Los Alamos National Laboratory for the determination of U and Pu by the tetrapropylammonium method. The absorbance of the U peak at 452.5 nm and of the valley at 460 nm are measured. Extraction with 2-nitropropane is recommended to eliminate Th interference. A sequential potassium permanganate/hydroxylamine treatment guarantees that all U is in the hexavalent state and reduces Ce(IV), Cr(VI), Mn(VII), and peroxide to noninterfering species. The concentration range initially measured with the automated spectrophotometer was 1 to 14 mg of U. The precision of the measurements was about 0.02-mg standard deviation, corresponding to an RSD of 2% at the 1-mg level and 0.2% at the 10-mg level. The automated instrument was also evaluated at lower levels of U (Ref. 231). Solutions containing from 0.12 to 1.5 mg were analyzed and a pooled standard deviation (for a single measurement) of 0.013 mg was found. The corresponding RSDs ranged from 10.4% at 0.12 mg of U to 0.87% at 1.5 mg of U.

Benzoyltrifluoroacetone

In an attempt to achieve higher precision in the determination of low levels of U with the Los Alamos automated spectrophotometer (Ref. 217), a method involving benzoyltriflouracetone (BTFA) as the chromogen is currently being evaluated. The nonautomated method has been described by Marsh (Ref. 218). The method involves the addition of a buffering and masking solution containing magnesium nitrate, cyclohexanediaminetetraacetic acid, hexamethylenetetramine, and nitric acid to the sample. The pH is adjusted to 5.6 or 5.7, and the U is extracted into BTFA/butyl propionate solution. The absorbance of the aqueous phase is measured at 384 and 400 nm. The relationship between absorbance and U content is linear in the range 5 to 85 g. The RSD ranged from 2.9% to 0.2%. Successful adaptation of the BTFA procedure to the automated spectrophotometer would make it possible to determine from 5 μg to 14 mg of U with a precision no worse than about 3% RSD at low concentrations and about 0.3% at the upper end of the range.

PAR and PAN

PAR and PAN are representative of a group of chromogens that form complexes with U that have very high molar absorptivities (Refs. 232 and 233). These are probably the most sensitive chromogenic reagents for U. Other reagents in this group that have been studied include 5-methyl PAN (Ref. 234), 2-(2-pyridylazo)-5-diethylaminophenol (PADAP) (Refs. 235 and 236), and 5-bromo PADAP (Refs. 237 and 238). These three reagents may not be readily available commercially. Since the procedures employing these chromogens are similar, the PAR method of Florence and Farrar (Ref. 239) will be used as an example.

PAR forms a 1:1 complex with uranyl ion at pH 8 in triethanolamine buffer. The molar absorptivity of the complex is 38,700 at 530 nm. Beer's law is obeyed to a concentration of 7 μg U/mL in the final solution. Both the free chromogen and the complex are water soluble. No extraction is required. The lowest concentration that can be determined using a 1-mL sample is 3 μg/mL. The precision of the method is about 1% RSD for samples containing more than 30 μg.

A mixed complexing solution containing (1,2-cyclohexylenedinitrilo) tetraacetic acid, sulfosalicylate, and fluoride effectively masks most interfering metals. The only serious interferences are V(V), Zr, Fe, Cr(III), and Si. Zirconium may be masked with meso-tartaric acid. Iron can be tolerated in amounts greater than 200 μg provided the absorbance is measured within 10 min of mixing. Vanadium(V) may be reduced with ascorbic acid to the tetravalent state, which interferes slightly. If large amounts of interfering impurities are known to be present, a preliminary separation of U is made, using a chelating-resin ion-exchange procedure. Detailed procedures may be found in Reference 240.

Other Chromogenic Agents

Two recent methods using other chromogenic agents for U determination are of interest for safeguards analysis.

The first method is specifically designed for measuring the U(IV) concentration in Purex process solutions. Uranium (IV) nitrate is frequently used as a reductant for Pu(IV) in the partition cycle for separating Pu from U. In the procedure of Gopalakrishnan et al. (Ref. 241), U(IV) is extracted from 0.5*M* HNO_3 medium with thenoyltrifluoroacetone (TTA) in benzene. Hydroxylamine hydrochloride and ascorbic acid are present as holding reductants for Pu(III) and Fe(II) in the aqueous phase. When the U(IV) concentration in the organic phase is 0.2 to 1.4 mg/mL, the absorbance of the $U(TTA)_4$ complex is measured at 660 nm against a TTA/benzene blank. When the aliquot of the organic phase contains 25 to 250 μg of U(IV), it is added to thorin reagent in 75% alcohol. The absorbance of the U(IV)/thorin complex is measured at 535 nm. The precisions of both procedures are 2% RSD.

Jablonski and Leyden (Ref. 242) have developed a continuous flow monitor for U in carbonate solutions, based on the reaction between U(VI) and 2,3-dihydroxynaphthalene-6-sulfonic acid. The relationship between absorbance and U concentration was linear for concentrations up to 100 μg/mL. The lower detection limit was 3.5 μg/L. The precision at 8 μg/mL was 9.9% RSD, improving to 1.1% at 60 μg/mL. The principal interference was Fe(II). Large quantities of Ca give low results, and large amounts of vanadate or molybdate give high results.

Survey of Production Facilities

The two methods most frequently used at production facilities for the determination of U in low-level process and waste solutions are spectrophotometry and fluorometry (see section 4.7.7). Very little routine performance data are available for either method, however. Two spectrophotometric methods are reported.

Two laboratories report methods in which the dibenzoylmethane [illegible]plex is measured. The first laboratory analyzes low-level liquid [illegible]rge solutions by first adding fluoride ion to mask the tetravalent ca[illegible] of Hf, Pu, Sn, Th, Ti, and Zr. Excess fluoride is masked with [illegible]$O_3)_3$ and Nb is masked with oxalate. The complex is measured at 416 nm in 2-mm cells. A six-point calibration curve ranging from 0 to 4 μg U/mL is checked each shift by running a 2-μg U/mL control standard. The random measurement error of replicate control standard determinations is 2% RSD. For process solutions of 0.2 to 50 μg/mL the random measurement error, based on duplicate sample measurements, is 76% RSD. A systematic measurement error of 0.51% RSD was determined by statistically combining the random error of the mean of the control standard measurements and the total uncertainty associated with the standard itself. The second laboratory employs a tributylphosphate/heptane-EDTA solvent extraction procedure to purify low-level scrap solutions preliminary to sample measurement at 410 nm. A random error of 0.6% RSD was obtained for the method from replicate measurements of control standards over a 2.5-yr period. No systematic error was reported.

A second method in which the peroxide complex is measured was reported by two laboratories. The first laboratory analyzes low-level ADU filtrate solutions by extracting first into TBP/hexane solution and then back into Na_2CO_3/NH_4OH solution. The peroxide complex is measured at 400 nm in a 1-in test tube. A 5-point calibration curve of 0 to 50 μg U/mL is checked each shift with a 20-μg U/mL control standard. The random error (including bulk sampling error) of the method for ADU filtrate samples at 68 μg U/mL is 4.0% RSD. No control measurement data are available. The second laboratory employs several methods for purifying various scrap solutions prior to measurement of the peroxide complex at 410 nm. The random error of replicate measurement of control standards over a 2.5-yr period was 0.4% RSD. No systematic error was reported.

Survey of Exchange Programs

This method was not evaluated.

4.7.7 Fluorometry

Description of Method

Uranyl salts fused in sodium fluoride exhibit a characteristic yellow-green fluorescence when excited by ultraviolet light. The fluorescence spectrum consists of four bands, of which the most intense is at 555 nm. The wavelength of most efficient excitation is at 365 nm. The fluorescence of U has been made the basis of a highly sensitive and specific method for its determination. The detection limit for U in a flux containing greater than 90% sodium fluoride is estimated to be about 10^{-7} mg. In such a flux, no other elements have been found to give a detectable fluorescence under the specified conditions of excitation and measurement of fluorescence. The intensity of the fluorescence for trace amounts of U is directly proportional to the amount present.

Unfortunately many common ions interfere by decreasing the fluorescence of U. This effect is termed "quenching." For this reason U is usually separated by extraction prior to fluorometric determination. Alternatively, the method of standard additions can be used.

The organic solvents used most extensively for separation of small amounts of U prior to its fluorometric determination have been TBP in an inert diluent, ethyl acetate, methyl isobutyl ketone, and TOPO. Acid-deficient aluminum nitrate solution (Ref. 243) is often added as a salting agent to facilitate the extraction. It has the advantages of masking fluoride and providing high ionic strength. A very selective separation is obtained when U is extracted as the tetrapropylammonium uranyl trinitrate salt into methyl isobutyl ketone (hexone) from an acid-deficient aluminum nitrate salting solution (Ref. 244). Boase and Foreman have described an anion-exchange separation (Ref. 88).

An aliquot of the purified U fraction is evaporated to dryness and the residue is fused with a measured quantity of flux. The composition of the fluxes used has ranged from 90% sodium carbonate/10% sodium fluoride to pure sodium fluoride. High carbonate fluxes have lower melting points than fluoride fluxes, permitting more reproducible fusion and easy removal of the melts from the fusion vessel. Major disadvantages of these fluxes are lower sensitivity, more pronounced quenching, and a hydroscopic property. The 98% sodium fluoride/2% lithium fluoride flux advocated by Centanni (Ref. 245) appears to be the optimum composition. A detailed review of the advantages and disadvantages of different fluxes is given in Reference 9, pp. 127-132.

Fusions are usually made in platinum dishes. Fusions have been performed with Meker burners (Ref. 246), Fletcher burners (Refs. 245 and 247), and furnaces, both automated (Refs. 248 and 249) and nonautomated (Ref. 88). The pellet, after cooling, is excited with an ultraviolet source. The fluorescence at 555 nm, which is proportional to the amount of U, is measured with a fluorophotometer. Uranium fluorescence is converted to U concentration by comparison with a calibration curve. Unknown samples are usually analyzed in duplicate or triplicate, and standard samples are analyzed at the same time.

The fluorescence of U in solution has been studied (Refs. 9 and 250) and found to be much less sensitive than fluorescence in fused pellets. Recently, however, a laser fluorometric method (Ref. 252) has been described that is simpler, more sensitive, and more rapid than the pellet fusion method. The method is direct and requires no separations, extractions, or fusions. The commercially available laser fluorometer employs a pulsed nitrogen laser that emits at 337 nm. The U sample is added to a proprietary buffered pyrophosphate reagent, which causes the U to emit a green luminescence when exposed to the light from the laser. A green filter between the sample cell and the photomultiplier tube removes the blue fluorescence from organics. Longer wavelengths will still be transmitted, however. The instrument has electronic gating circuitry that waits for other fluorescence from organics to decay before the longer lived U phosphorescence is measured. A standard addition technique is used to overcome sample matrix effects.

Scope of Applications

The fluorometric techniques are applied to the determination of trace quantities of U in aqueous or organic solutions resulting from the processing of irradiated reactor fuels, and in other waste solutions.

Summary of Performance

Table 4.24 summarizes the performance of the method as applied to v ous low-level U waste solutions. In general, the method employs a p liminary extraction to remove interfering impurities, followed with a

Table 4.24 Summary of performance: fluorometric determination of uranium

Application	Method	Performance (% RSD)		Source[a]
		Random Error	Systematic Error	
Low-level uranium solutions	Tetrapropylammonium complex extraction, fuse with 98% NaF/2% LiF, 5μg U/mL	13	—	L
	Ethyl acetate extraction, fuse with $NaKCO_3$/NaF 0.1 to 0.5 mg/g	5 to 6	—	L
	Ethyl acetate extraction, 0.05 to 50 μg U/g	11.3	—	L
	Direct, laser fluorometric, 0.05 to 50 μg U/g	5.3	—	L
	Tetrapropylammonium complex extraction, fuse NaF, 0.2 μg U	7.2	—	U
	TOPO extraction, fuse in 98% NaF/2% LiF flux, 0.005 to 100 μg U/g	51 to 3.1	—	U
	Standard additions (internal spike), fuse with 98% NaF/2% LiF, 10 μg U/mL	14	3.6	U
Grinder water with suspended solids	Standard additions (internal spike), fuse with 98% NaF/2% LiF, 2000 μg U/g	23[b]	5.8	U

[a] L = literature survey; U = users' survey of production facilities.

[b] Includes sampling error.

TOPO = tri-n-octylphosphine oxide

NaF fusion. The laser fluorometric and standard addition methods, however, are used without the preliminary treatment. In addition, the laser method eliminates the fusion step. Specific method applications are discussed later in this section.

Equipment

(1) Fluorometer. A commercial fluorometer for use with fused pellets has an excitation wavelength of 365 nm, measures the fluorescence at 555 nm, and is capable of detecting 0.5 ng U. The Galvanek-Morrison design is available from Jarrell-Ash Co., Waltham, Mass. Improvements to the fluorometer (modification of the amplifier circuit and the response linearity; substitution of a digital voltmeter for the microammeter) have been described (Ref. 253). The laser fluorometer (Scintrex Ltd., Concord, Ontario, Canada) for the direct analysis of solutions uses a low-power sealed nitrogen laser emitting at 337 nm. The detection limit was found to be 0.005 ng U (Ref. 252). The instrument can measure U solution concentrations from 0.05 ng/g to 50,000 ng/g by the turn of a "sensitivity" control.

(2) Blast burner, muffle furnace, tube furnace, or induction heater capable of 950°C temperature. The widely used Fletcher burner is described in References 245 and 247. Modifications, consisting of a quick-opening valve, pilot light ignition, and a heat shield, are described in Reference 253. Strain (Ref. 249) has described an automated sintering furnace.

(3) Blender, P-K, Twin Shell, or equivalent for blending flux.

(4) Pelletizer, syringe-type, to deliver the appropriate amount of flux.

(5) Platinum dishes.

(6) Optical pyrometer, for determining the fusion temperature of the flux.

Major Sources of Error

The fluorescence in fused or sintered pellets is influenced by a number of factors: the composition of the flux, weight of flux, pellet thickness, fusion time and temperature, cooling time, the reflectivity of the dish, and the time elapsed between fusion and measurement. Studies and reviews of these and other factors may be found in References 9, 245, 246, 247, 250, and 251.

Because the method is used for the determination of micro quantities of U, the presence of small quantities of that element in the ingredients of the flux and in other reagents can lead to serious errors. Each batch of flux and all reagents must be checked to ensure that if any U is present the quantity in a reagent blank is very much smaller than the quantities to be measured in samples. Every effort must be made to prevent U contamination.

Strain (Ref. 249) recently studied factors affecting the precision of the pellet method. His equipment included an automated sintering furnace and an automated fluorometer (Ref. 248). He concluded that the major remaining factors that limit precision are nonuniform loading of U on the pellet and the variation in reflected fluorescence caused by surface irregularities in the Pt dishes used for sintering and measurement. The second source of variation can be eliminated by transferring the sintered pellet to a holder of uniform surface, either nonreflecting or totally reflecting, prior to measuring the fluorescence.

Sources of error in the direct laser fluorometric analysis of solutions (Ref. 252) are changes in temperature during and between measurements (the intensity of fluorescence decreases with increasing temperature) and errors in pipetting or weighing the small sample aliquots.

The fluorometric method is highly specific for U, since no other element has been found to give a detectable fluorescence in high (>90%) sodium fluoride fluxes under the specified conditions of excitation and measurement of fluorescence. However, serious interference is caused by components that quench the fluorescence of U. Metal ions that seriously quench include Cd, Cr, Co, Cu, Fe, Mg, Mn, Ni, Pb, Pt, Pu, Si, Th, W, V, and Zn. The preliminary extraction with tetrapropylammonium nitrate (Ref. 244) into hexone selectively separates U from these and other cations. Schoenfeld (Ref. 246) found that extraction with ethyl acetate gave insufficient separation from many impurities and that the method of standard additions was necessary to compensate for matrix effects. Jarozeski and Gregy (Ref. 254) studied the determination of 0.04 μg of U in Pu-U mixtures having up to 20:1 ratios of the two elements. Samples were analyzed without pretreatment or separation. No interference was found.

Anions can interfere by inhibiting the extraction of U (Ref. 244 and 255). Large amounts of sulfate precipitate Al as aluminum sulfate in the salted aqueous phase. The precipitate carries U to cause low recovery. High concentrations of hydrochloric acid also decrease the recovery of U (Ref. 255). The tolerance for acid is 3 meq in the sample aliquot. If excessive amounts of sulfate, chloride, or acid are present, the sample aliquot should be evaporated to near dryness and redissolved in 6*M* nitric acid before extraction.

The only fission product that is measurably extracted into hexone is ruthenium. The Ru alloys with the Pt dish during fusion, resulting in a buildup of beta activity, mainly from ^{106}Ru ($t_{1/2}$ = 1 yr). For this reason a separate set of Pt dishes should be used for the analysis of highly radioactive samples. These dishes should be checked periodically for radiation buildup and set aside if radiation levels become excessive.

In the laser fluorometric analysis of solutions, interferences are avoided by the gating system of the instrument and by making standard additions.

Measurement Control Requirements

The fluorometer is calibrated by carrying standard solutions covering the concentration range of interest through the entire procedure. A calibration curve is constructed by plotting the weight (or concentration) of U versus the fluorescence reading corrected for reagent blank. Procedures for calibration are given in References 10 and 256. It is necessary to recalibrate the fluorometer whenever any change is made in the fluorometer, reagents, or fusion conditions. The calibration should be rechecked daily with standards (analyzed in duplicate or triplicate) that bracket the expected concentration range.

Data Analysis Requirements

Calculations for fluorometry are simple and straightforward. The determination of U in aqueous solutions by extraction into hexone and measurement of the fluorescence of a fused pellet may be calculated as follows:

$$U = \frac{PM}{OS} \tag{4-32}$$

where

U = concentration of uranium, mg/mL
P = uranium in pellet (from calibration curve), mg
M = volume of hexone used for extraction, mL
O = volume of organic phase pipetted onto pellet, mL
S = volume of sample aliquot, mL

In the laser fluorometric analysis of solutions, the concentration of U in the sample is calculated by the following equation:

$$U = \frac{WF_1S_1}{Z(F_2S_2 - F_1S_1)} \tag{4-33}$$

where

U = concentration of uranium, g/g sample
W = uranium added in the standard addition, g
F_1 = fluorescence of solution S_1
S_1 = total solution in the cuvette at F_1: water plus fluorescence agent plus sample, g
F_2 = fluorescence of solution S_2
S_2 = total solution in the cuvette at F_2: water plus fluorescence agent plus sample plus standard addition, g
Z = sample added to cuvette, g

Survey of Selected Literature

Values for the accuracy and precision of the fused pellet method given by different investigators vary widely, depending upon the procedure and the types of samples analyzed.

A recent comparison (Ref. 252) of the fused pellet method with the laser fluorometric analysis of solutions yielded some interesting values. Ethyl acetate was used to extract U prior to pellet fusion. Four U standards, with 0.05, 0.5, 5, and 50 μg U/g, were analyzed in triplicate by each method. Recoveries for the fused pellet method ranged from 62.1% to 104.4%, with a mean of 90.2 ± 6.4% (95% confidence interval, 12 degrees of freedom). For the laser fluorometric method, recoveries ranged from 92.8% to 106.5%, with a mean of 101.9 ± 2.3% (95% confidence interval, 13 degrees of freedom). The bias was statistically significant for the fused pellet method, but not for the laser fluorometer method. The standard deviation of the relative differences for the U standards analyzed by the laser fluorometer method was 5.3%, as compared to 11.3% by the fused pellet method.

A method that involves separation of U as a tetrapropylammonium nitrate complex and fusion of an aliquot of the organic phase with 98% NaF/2% LiF flux is applicable to quantities of 2.5×10^{-6} to 5×10^{-3} mg of U. As the procedure is written (Ref. 10, pp. 398 through 403), this corresponds to 5×10^{-5} to 1×10^{-1} mg U/mL for aqueous samples. For organic samples, it corresponds to 2.5×10^{-5} to 5×10^{-2} mg U/mL. The precision of the method at the 5×10^{-3} mg/mL level is about 13%. A bias of -2 ± 9% was calculated from the results of four laboratories (Ref. 152).

Another method involving an ethyl acetate extraction and fusion with sodium potassium carbonate/sodium fluoride fusion mixture was applied to low-grade U waste products (Ref. 10, pp. 232-237). The samples contained 0.001% to 1% U. The precision on samples containing 0.01% to 0.05% U was 5% to 6% RSD.

The laser fluorometric method (Ref. 252) is applicable to samples containing from 0.05 ng/g to 50,000 ng/g. A precision and accuracy of 2% to 3% relative are claimed. The method is rapid; four samples can be analyzed in duplicate in 1 h.

The fused pellet method, as used by NBL (Ref. 252), required a minimum elapsed time of 8 h; groups of 15 samples took 3 days, including preparation and cleanup time. Workers at Oak Ridge were able to reduce the analysis time for 16 samples by the pellet method to about 1.5 h with an automated sintering furnace (Ref. 244) and an automated fluorometer (Ref. 248).

In routine use, the fused pellet method may be expected to have a precision of 10% to 20% RSD. The lower value may be attained by careful control of all factors and perhaps improved by use of automated equipment (Refs. 248 and 249).

Survey of Production Facilities

The two methods most frequently used at production facilities for the determination of U in low-level solutions are fluorometry and spectrophotometry (Section 4.7.6). Very little routine performance information is available for either method. However, three fluorometric methods that are used are discussed in the following paragraphs.

In one application, approximately 2-μg/mL U solutions are analyzed by first extracting a 1-μg U sample with tetrapropylammonium nitrate in hexone to remove quenching impurities. A 0.2-μg, or less, U aliquot is fused with NaF, the fluorescence measured, and the U concentration read out directly. Calibration standards are measured each shift to set up the instrument for direct readout. Approximately 20 control standards are measured per quarter to ensure reliable operation. The random error of the method is 7.2% RSD based on duplicate determination of samples.

In another application, UNH and tap water solutions are analyzed by first extracting an aliquot with TOPO in mineral spirits. A 0.001- to 5-μg U aliquot is fused in 98% NaF/2% LiF flux, fluoresced, and read directly in μg U/mL solution. Method performance is checked weekly by measuring control standards. The random error of the method for 0.005- to 100-μg U/g UNH solutions ranges from 3.1% to 12% RSD. For 1 μg U/g tap water samples, a relative standard deviation of 51% was obtained.

A standard additions method has been applied to the determination of U in 10-μg/mL uranium solutions and 2000-μg/mL grinder water with suspended solids. Samples containing 0.01 to 10 μg U are spiked with different amounts of NBS standard solution and fused with 98% NaF/2% LiF flux. Control standards are analyzed periodically to ensure measurement reliability. The random error of the method applied to the determination of 10-μg/mL U solutions is 14% RSD. A systematic error of 3.6% RSD is based on the random error of the mean of the control standard measurements. A random error of 23% RSD was obtained for grinder water at 2000 μg/mL with a systematic error of 5.8% RSD.

Survey of Exchange Programs

This method was not evaluated by these programs.

4.8 DETERMINATION OF URANIUM ISOTOPIC ABUNDANCE

4.8.1 Surface-Ionization Mass Spectrometry

Description of Method

The preferred and most widely used technique for determining the isotopic composition of U is surface-ionization mass spectrometry. In general, this method is applicable to the isotopic analysis of U in many U-compounds and alloys after dissolution and chemical treatment to obtain purified U fractions. The sample size required for an analysis is 10^{-8} to 10^{-5} g of U, depending on the sensitivity of the instrument.

The purified U fraction is diluted and an aliquot is evaporated on the mass spectrometer filament. A current is passed through to form an adherent U oxide, preferably the yellow U trioxide, and to remove acid, water, and some organic matter. The filament assembly is placed within the ion source of the mass spectrometer and outgassed. The filament(s) then are heated following a carefully selected heating pattern to vaporize and ionize U. The singly charged metal ions produced by this thermal ionization are accelerated and focused with an electrostatic ion lens into the mass-analyzer section. The total ion beam is separated according to the mass-to-charge ratio (m/e) of the ions. By an appropriate variation of the magnetic field(s) and/or the accelerating potential, the separated ion beams are sequentially focused on the detector, which is either a Faraday cup, an electron multiplier, or a photomultiplier detector. The detector current or pulses are further amplified and recorded as a function of the mass on a stripchart recorder or by a digital recording system. The peak currents (intensities) at each isotopic mass are measured, and the average isotopic ratios are calculated with reference to the ^{238}U or ^{235}U peak intensity.

These ratios are corrected for nonlinearities in the detector/recording system and for the mass discrimination of the mass spectrometer. From the corrected isotopic abundance ratios, the isotopic composition of U is calculated in atom percent and weight percent. Alternatively, rather than compute isotope ratios, one may correct the measured intensities for nonlinearities and mass discrimination and then normalize all intensities.

With an automated scan capability, a sample-introduction lock, high-speed pumping system, and digital data acquisition and reduction, two operators can process between 12 and 16 samples per day; however, this is peak output. It is more realistic to expect the analysis of 7 to 9 samples per day (or per shift). A detailed procedure is described in References 257 and 258.

Scope of Applications

The method is applicable to a variety of physical and chemical forms of U ranging from high-purity UO_2 to spent fuel dissolver solutions. However, spent fuel dissolver solutions are more commonly analyzed by isotope dilution mass spectrometry because the U concentration as well as the U isotopic abundances are desired. The sample to be analyzed contains the high purity U fraction separated from solutions prepared by dissolution of U oxides, U metal and alloys, mixed U-Pu oxides, and such samples as nuclear fuels clad with Al, stainless steel, or Zircaloy.

The recommended method (Refs. 257 and 258) is applicable to a quantity of U in the range of 10^{-8} to 10^{-5} g per determination. However, a quantity of the U compound is taken for dissolution and purification (if necessary) to give a final U concentration of 1 to 10 mg/mL in a volume of 10 mL.

Summary of Performance

Table 4.25 summarizes the performance of the method as applied to a wide range of pure feed, product, and solution samples. The method was also applied to ash and scrap material. Random error includes isotopic sampling errors in certain cases and is quite evident for the ash and U_3O_8 subblend (blend of different enrichments) materials.

The random error listed is normally a single reported value for a particular material type and enrichment. Some values are reported as unweighted averages and a range of performances of the different laboratories on similar materials. Specific method applications are discussed later in this section. These discussions will correspond respectively to the literature, user, and exchange source categories listed in the table.

Equipment

Mass Spectrometer

The minimum specifications for the mass spectrometer required for this procedure are as follows:

(1) Ion source
  (*a*) Thermal ionization source with triple filament assembly. A single, V-shaped filament is acceptable with an ion-counting detection system.
  (*b*) Filament current supply stabilization of one part in 10^4 or better.
  (*c*) Pyrex or quartz filament viewing window.
(2) Mass analyzer
  (*a*) Mass resolution of 600 or better at mass 238.
  (*b*) Abundance sensitivity of at least 20,000 at a resolution of 600 and with a pressure of less than 5×10^{-8} torr in the analyzer (flight tube). Abundance sensitivity is measured at mass positions 238 and 237 on a spectrum generated from natural U.
(3) Vacuum
  (*a*) Minimum vacuum of 5×10^{-8} torr in the analyzer and 1×10^{-7} torr in the ion-source chamber.
  (*b*) Pumping speed sufficient to maintain a vacuum of better than 5×10^{-8} torr during analysis [while filament(s) are hot].

   (*c*) Differential pumping of ion-source chamber and analyzer with isolation valve (beam valve) between ion-source chamber and analyzer.
   (*d*) Vacuum lock sample insertion with sample carriage or multiple-source holder system.

(4) Detection system
   (*a*) Overall instrumental sensitivity of 1×10^{-9} A · s/μg or better; i.e., peak intensity for the ^{238}U isotope of at least 1×10^{-12} A (measured at input to electron multiplier) for an average duration of 1000 s for a filament loading of 1 μg of U with specified gain and 1-s time constant.
   (*b*) Electron multiplier primary detector with stable current gain of 10^5, or, equivalent scintillation photomultiplier tube; electron multiplier operating mode—either pulse counting or dc current (integrating).
   (*c*) Data logging system according to user preference, but should include oscilloscope or stripchart recorder to view peaks when tuning spectrometer.

Mass Spectrometer Accessories

(1) Filament material of high-purity, electron beam zone-refined rhenium, tungsten, or tantalum
(2) Filament-forming jig
(3) Filament assemblies (hats)
(4) Spotwelder
(5) Filament-loading unit
(6) Filament bakeout chamber, capable of heating to 2000°C under vacuum of better than 1×10^{-6} torr for outgassing of filament
(7) Optical pyrometer, range to at least 2500°C

Cost

Surface-ionization instruments with a single-stage magnetic analyzer, Faraday cup, and/or electron-multiplier detector and stripchart recorder can be purchased for approximately $100,000, depending on accessories. Automation systems for peak stepping and digital data acquisition and reduction are $25,000 to $40,000. Tandem magnetic analyzer instruments employing pulse-counting detection with automated mass-scanning provisions and digital data acquisition and reduction are priced at about $150,000. Accessories such as gloveboxes, auxiliary vacuum systems, and clean benches can add another $10,000 to $50,000 to the cost of the mass spectrometric facility.

Table 4.25 Summary of performance: surface-ionization mass spectrometric determination of uranium-235

Application	% ^{235}U	Performance (% RSD)		Source[a]
		Random Error	Systematic Error	
Pure uranium standard solutions	1.5	0.2, 0.4	—	L
	1 to 50	0.15	0.063	U
	1.5 to 4	0.14	0.061	U
	3.0	0.067 (0.018 to 0.14)	0.054	U
	49.4	0.009, 0.029	0.052	U
	92	0.02	—	L
	93.3	0.00[illegible], 0.007	0.005	U
	97.7	0.013 0.005 to 0.032)	0.004	U
Pure uranium process solutions	3.0	0.083[b]	0.062	U
	89	0.001[b]	0.003	U
	93	0.01	—	U
	97	0.015[b]	0.003	U
Uranyl nitrate solution	2.8	0.40[b]	0.059	U
	3	0.17 (0.048 to 0.44)	—	E
	2 to 5	0.1	—	U
	54	0.038	—	U
	93	0.026	—	U
UF_6	0.7	0.66 (0.036 to 1.8)	—	E
	1.7	0.38 (0.029 to 0.88)	—	E

Note—See footnote at end of table.

Table 4.25 Summary of performance: surface-ionization mass spectrometric determination of uranium-235 (Cont'd)

Application	% ^{235}U	Performance (% RSD)		Source[a]
		Random Error	Systematic Error	
UF_4	93	0.032	—	U
UO_2 powder	2.8	0.12, 0.28[b]	—	U
	2.5 to 3	0.22 (0.046 to 0.68)	—	E
UO_2 pellets	2.8	0.41[b]	0.059	U
U_3O_8 powder	20	0.11	—	U
	93	0.019	—	U
	2.8 (subblend)	4.3[b]	0.059	U
U metal	93	0	—	U
U alloy	97	0.008	0.008	U
(U,Pu) carbide	72	0.014[b]	0.052	U
(U,Pu) carbide, oxide	38	0.31[b]	0.051	U
(U,Pu) oxide powder	0.7	0.58 (0.51 to 0.66)	—	E
(U,Pu) oxide pellets	0.7	0.94	—	E
HTGR/TRIGA feed	20	0.16[b]	—	U
	70	0.07[b]	—	U
ATR/TRTR material	93	0.008[b]	0.052	U
Ash	2.8	1.9[b]	0.059	U
Scrap	97	0.015[b]	0.003	U

[a] E = survey of exchange programs; L = literature survey; U = users' survey of production facilities.

[b] Includes sampling error.

Major Sources of Error

A detailed discussion of sources of error and interferences is given in References 257 and 258. This section includes only an abbreviated account of the principal factors that need to be considered.

Source Discrimination

Thermally produced ions of the lighter isotopes are vaporized and ionized more readily than the heavier isotopes of the same element. Fractionation is a complex, time-dependent phenomenon. A reproducible analytical procedure must be strictly followed. Such a procedure will keep under control such factors (Refs. 142 and 259) as filament temperature, filament loading, acidity of the sample, chemical form and oxidation state of the element, sample mounting procedure, outgassing procedure, and heating pattern and temperature.

Ion-Optical Discrimination

The ion lens and the magnetic sector mass analyzer are not perfect. As a result, the ion path from the exit slit of the ion source to the entry slit of the ion collector/detector is not exactly the same for all ions of a given m/e. To minimize this effect, a high accelerating potential and a large ion-transmission coefficient are desirable (Ref. 260). Again, it is necessary to reproduce the spectrometer operating conditions for sample and standard, or for successive filament loadings of the same sample. This includes the mechanical alignment of the filament assembly in the ion source, focus of the ion lens, scanning mode, and scanning rate.

Electron-Multiplier Discrimination and Nonlinearities in the Ion-Current Amplification and Recording System

The procedures given in the two manuals listed in References 257 and 258 contain calibration procedures to correct the measurements for these sources of error. Corrections for source, ion-optical, and electron-multiplier discriminations have been combined when establishing the mass discrimination factor. This factor is determined using NBS U standards, principally U-500.

Interferences

The accurate mass spectrometric determination of the isotopic composition of U depends on the absence of ions with the same nominal mass as the measured U ions and the absence of impurities that cause erratic ion emission. Normally such interfering substances are absent from high-purity U metal and compounds. For other materials, in particular for those containing Pu, a chemical treatment must be used to provide a high-purity U fraction for analysis.

Significant errors may be introduced into the results unless great care is exercised to prevent sample-to-sample contamination during chemical pretreatment and preparation. Also, U can be a common environmental contaminant in nuclear laboratories. Therefore, scrupulous housekeeping in the working areas is absolutely essential.

The filament material, all reagents, and reagent storage containers should have low levels of U since they may contribute to the instrument background at the U isotopic mass positions. It is recommended that the background of the instrument system be obtained when a new batch of reagents or filament material is used. If the background is unacceptably high, purer filament material and/or reagents should be obtained.

Interferences may also be caused by source memory. Memory effects are due to the deposition of material on the focusing plates and the ion-source slits. Some of the surface deposits are sputtered off during the analysis of the next sample and are ionized and mass analyzed along with the sample. If at all possible, U and Pu samples should be analyzed on separate instruments, or at least in separate groups. Also, samples with low and high ^{235}U enrichment should be analyzed separately in groups to prevent biased results. To minimize memory effects, it is recommended that the high-voltage parts of the ion source be replaced with clean ones before analyzing a new group of samples with an enrichment differing from that of the preceding group.

Measurement Control Requirements

At least once during each shift the NBS standard with an enrichment nearest to the enrichment of the samples should be analyzed. If a suitable NBS U standard is not available, the quality control laboratory should retain a quantity of an appropriate production lot, preferably in powder form. This lot should be characterized initially to give reliable estimates of the isotopic composition. Subsequently, samples from this designated lot can serve as an "in-house" standard. Alternatively, a suitable standard may be blended from NBS reference materials.

Control charts for the average value for each isotopic ratio and for the range of these ratios from each filament loading should be established. When the average value of $^{235}U/^{238}U$ changes at the 0.05 significance level, the cause(s) for such shifts should be investigated before continuing with the analysis of samples. It is recommended that a second NBS standard be run immediately after an "out-of-limit" situation arises. This eliminates operator error as a possible cause for the problem.

Data Analysis Requirements

Raw isotopic data, normally obtained from a digital or stripchart recording system, must be corrected for nonlinearities in the detector/recording system and for the mass discrimination of the mass spectrometer. From the corrected isotopic (peak) intensities, uranium isotopic composition may be calculated as atom percent, weight percent, or as a ratio of one isotope to the ^{238}U or ^{235}U (major) isotope. The calculations are relatively straightforward and can be performed on a desk top calculator. A computer is recommended, however, for large numbers of analyses. Detailed procedures for calculating isotopic compositions may be found in References 142, 257, 258, 261, 262, and 263.

Survey of Selected Literature

This method is applicable to the determination of the absolute composition of U. Two of the mass spectrometric techniques that may be applied are single- and multiple-filament surface ionization. The single-filament method is suitable for U samples containing more than 5×10^{-5} g. The multiple-filament method and electron-multiplier detection is suitable for samples with U levels in the range of 10^{-7} to 10^{-4} g (the preferred procedure). The method can be extended to samples containing less than 10^{-7} g U if essential "U-free" reagents and glassware (quartz) are employed. The procedure is applicable to U in any of the common forms, pure or alloyed, irradiated or unirradiated, or as most of the common compounds encountered in the nuclear fuel cycle.

The precision attainable varies with the relative abundance of each isotope. Approximate relative standard deviations obtained in the isotopic analysis of U are given in Table 4.26. The number of observations averaged will also affect the precision.

Table 4.26 Isotopic analysis of uranium

Isotope	Relative Abundance (weight %)	% RSD
^{234}U	0.001 to 0.01	5
^{235}U	1 to 5	0.2
^{236}U	0.01 to 0.1	3
^{238}U	95 to 100	0.1

Additional reliability information may be obtained from the values reported by 11 laboratories that participated in a method-evaluation program organized by NBL. Two blends prepared from NBS isotopic U standards were analyzed, one containing 92 weight percent ^{235}U, the other 1.5 weight percent ^{235}U. Duplicate or triplicate measurements were made on each sample by each laboratory over a short time interval (Ref. 152).

Figure 4.8 is a plot of the relative within-laboratories standard deviation (RSD_w) as a function of the isotopic abundance of ^{234}U, ^{235}U, and ^{236}U.

Survey of Production Facilities

Table 4.27 lists the performance of the surface-ionization technique at production facilities as applied to various material types and enrichments. The random measurement error typically runs less than 0.2% RSD for low-enriched (approximately 3% ^{235}U) standard or non-production type materials. Similar materials with enrichments greater than 50% yield measurement random errors less than 0.04% RSD. Production materials typically experience higher random errors due to sampling and/or sample preparation procedures.

The basic method employs a triple filament source configuration with single focusing, electron-multiplier detection, and magnetic scanning. Several facilities also employ automated data acquisition and calculation. Table 4.27 describes some of these method variations.

Instrument calibration factors are determined and calibration verification measurements are made by analyzing one or more of the NBS isotopic standards. Mass discrimination factors are normally determined when the routine calibration verification measurements indicate an out-of-control situation or when an electron multiplier has been replaced. In certain cases, calibration factors are determined for each enrichment level. Calibration verification measurements are normally made in duplicate on a daily basis but not less than weekly during periods of operation.

Systematic errors are calculated by statistically combining the standard deviation of the mean determined from the replicate verification standard measurements and the total uncertainty of the standards certified value. Random errors are determined from replicate measurement of standard and production materials. Normally, the random error will include short-term systematic errors associated with day-to-day and operator-to-operator variations as these variations are considered to be part of the measurement method. In several cases bulk sampling error (inhomogeneity) is included as part of random error. This is because the particular sampling/analysis scheme used by a laboratory does not permit separating measurement and sampling errors. Table 4.27 lists the systematic and random errors of the method for several different materials. Figure 4.9 presents the random error in graphic form.

Survey of Exchange Programs

The surface ionization methods used in the SALE (Ref. 154) and GAE (Ref. 155) programs are not defined. They would be expected, however, to be similar to those described for the user facilities since several of the user facilities are also participants in the exchange programs.

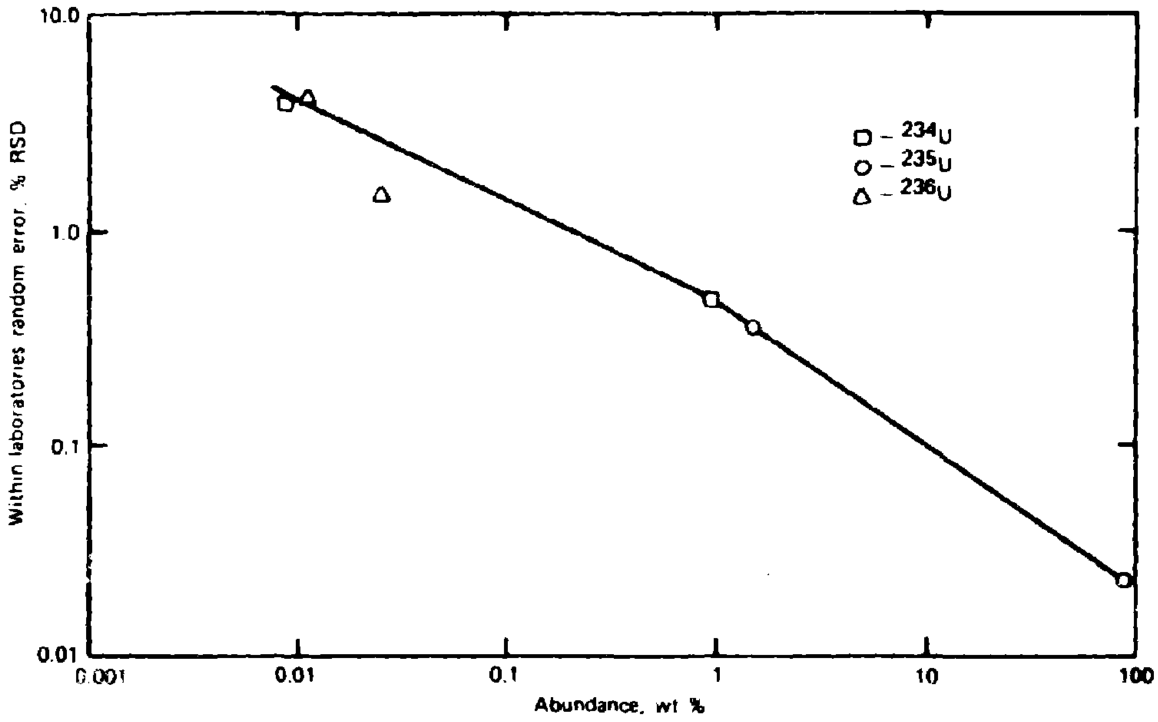

Figure 4.8 Precision of uranium isotopic abundance measurements.

Table 4.27 Surface-ionization mass spectrometric determination of uranium-235—performance at production facilities

Application	% ^{235}U	Method	Performance (% RSD)	
			Random Error	Systematic Error
Pure uranium standard solutions	1 to 50	15"/90° sector, e-multiplier	0.15	0.063
	1.5 to 4.0	12"/60° or 90° sector, e-multiplier, auto data acquisition	0.14	0.061
	3.0	High resolution, double focus	0.018	0.050
	3.0	12"/60° sector, Faraday cage	0.044	0.051
	3.0	High resolution, double focus	0.014	0.062
	49.4	High resolution, double focus	0.009	0.051
	49.4	12"/60° sector, Faraday cage	0.029	0.052
	93.3	High resolution, double focus	0.003	0.005
	93.3	12"/60° sector, Faraday cage	0.007	0.005
	97.7	12"/60° sector, Faraday cage	0.005	0.002
	97.7	—	0.009	0.003
	97.7	High resolution, double focus	0.007	0.003
	97.7	35 cm/90° sector, e-multiplier, auto data acquisition	0.032	0.008
Pure uranium process solutions	3.0	High resolution, double focus	0.083[a]	0.062
	89	High resolution, double focus	0.001[a]	0.003
	93	12"/60° sector, Faraday cage	0.01	—
	97	—	0.015[a]	0.003
Uranyl nitrate solutions	2.8	12"/60° or 90° sector, e-multiplier, auto data acquisition	0.40[a]	0.059
	2 to 5	12"/60° sector, Faraday cage	0.1	—
	54	35 cm/90° sector, e-multiplier, auto data acquisition	0.038	—
	93	6"/60° sector, e-multiplier, voltage scan, auto data acquisition	0.026	—

Note—See footnote at end of table.

Table 4.27 Surface-ionization mass spectrometric determination of uranium-235—performance at production facilities (Cont'd)

Application	% ^{235}U	Method	Performance (% RSD)	
			Random Error	Systematic Error
UF_4	93	6"/60° sector, e-multiplier, voltage scan, auto data acquisition	0.032	—
UO_2 powder	2.8	12"/60° or 90° sector, e-multiplier, auto data acquisition	0.28[a]	0.059
	2.8	12"/60° sector, Faraday cage	0.12[a]	—
UO_2 pellets	2.8	12"/60° or 90° sector, e-multiplier, auto data acquisition	0.41[a]	0.059
U_3O_8 powder	20	35 cm/90° sector, e-multiplier, auto data acquisition	0.11	—
	93	35 cm/90° sector, e-multiplier, auto data acquisition	0.019	—
	2.8 (subblend)	12"/60° or 90° sector, e-multiplier, auto data acquisition	4.3	0.059
U metal	93	35 cm/90° sector, e-multiplier, auto data acquisition	0.017	[illegible]
U alloy	97	35 cm/90° sector, e-multiplier, auto data acquisition	0.008	0.008
(U, Pu)C	72	12"/60° sector, Faraday cage	0.014[a]	0.052
(U, Pu) C, $(U,Pu)O_2$	38	High resolution, double focus	0.31[a]	0.051
HTGR/TRIGA feed	20	—	0.16[a]	—
	70	—	0.07[a]	—
ATR/TRTR material	93	12"/60° sector, Faraday cage	0.008[a]	0.052
Ash	2.8	12"/60° or 90° sector, e-multiplier, auto data acquisition	1.9[a]	0.059
Scrap	97	—	0.015[a]	0.003

[a] Includes sampling error.

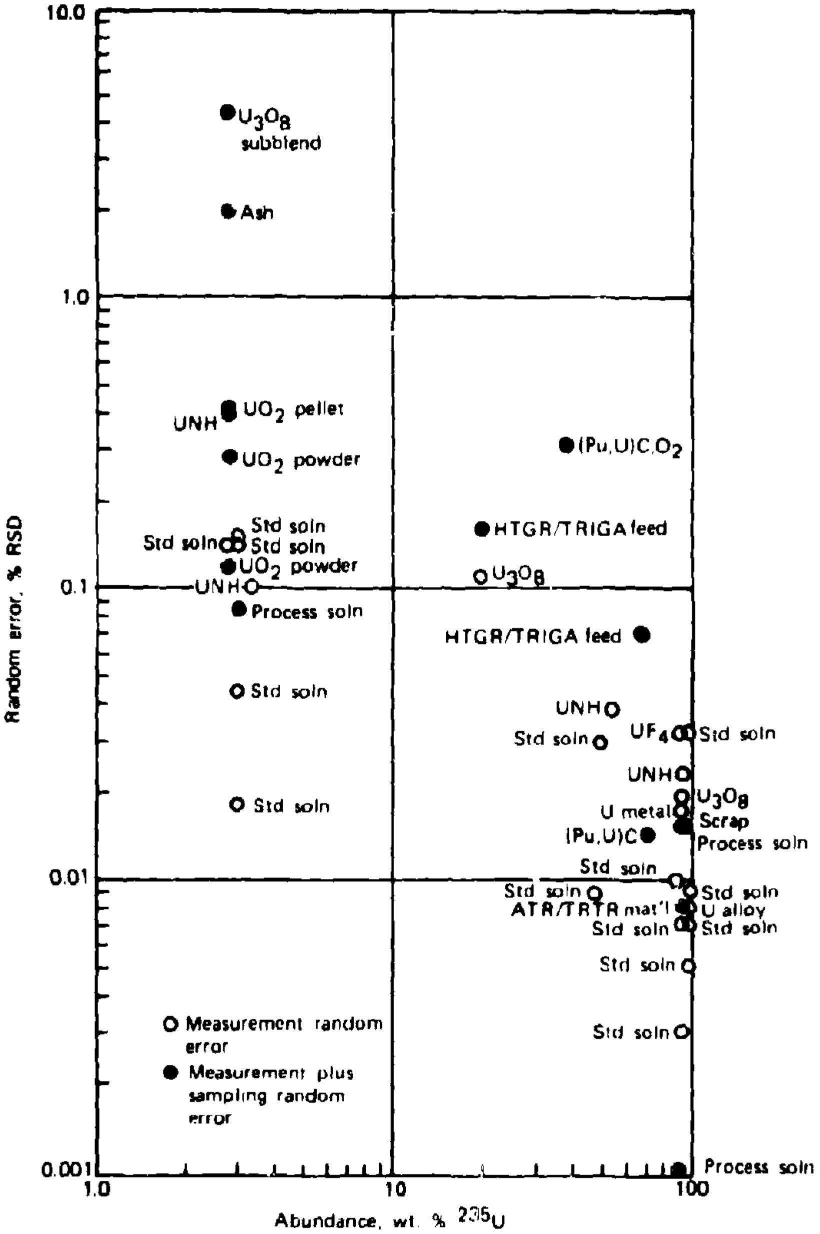

Figure 4.9 Surface-ionization mass spectrometry—performance at production facilities.

The method, as applied by the SALE participants to UO_2 powder and uranyl nitrate solutions at the 3% ^{235}U level, averages 0.22% and 0.17% RSD, respectively. A relative standard deviation of 0.58% and 0.94% was obtained for MOX powder and pellets, respectively, at the 0.7% ^{235}U level. Figure 4.10 presents the individual SALE laboratory results. Average random errors of 0.66% and 0.38% RSD were obtained by the GAE laboratories for UF_6 at the 0.7% and 1.7% ^{235}U levels, respectively.

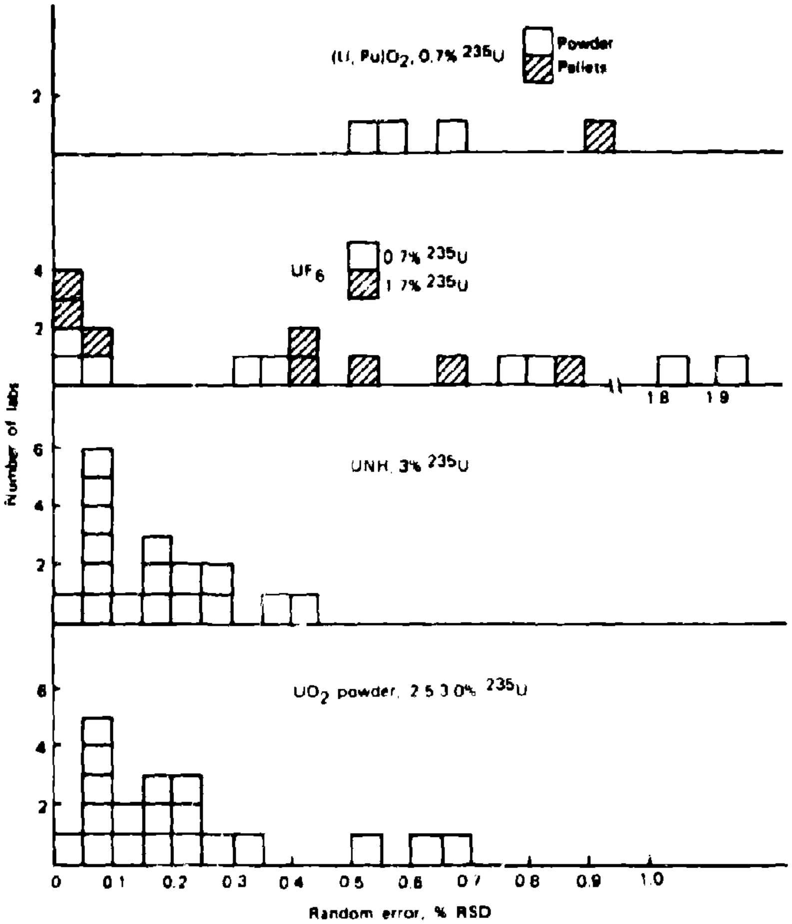

Figure 4.10 Surface-ionization mass spectrometry—exchange program performance.

4.8.2 Gas-Ionization Mass Spectrometry

Description of Method

Gas-ionization mass spectrometry is particularly useful for determining the isotopic composition of U in uranium hexafluoride (UF_6) since no chemical treatment other than purification is required prior to the analysis. The technique is most often employed at enrichment facilities. Gas-ionization mass spectrometry can be used for the analysis of any U compound that can be converted to UF_6; however, surface-ionization mass spectrometry is generally preferred for other compounds.

A comparison of the surface-ionization method with the gas electron bombardment method is given in Table 4.28. It can be seen that the gas-ionization technique requires a large sample and, therefore, is less than satisfactory for the analysis of materials that are highly radioactive or of limited availability. In addition, the gas-ionization technique is subject to a substantial memory effect. When a wide range of enrichments is to be determined, it is advisable to have a number of instruments, each dedicated to a narrow band of enrichments.

Table 4.28 Comparison of mass spectrometric methods[a]

Parameter	Surface Ionization	Gas Electron Bombardment
Sample size	10^{-8} to 10^{-5} g	10^{-1} g
Sample form	Nitrate, oxide, metal	UF_6
Precision	0.1% to 1.0%	0.01% to 0.1%
Memory effect	Less than 0.01%	1% to 10%
Purity requirements	Can be analyzed with up to 20 times other metals present provided there is no mass interference	High purity UF_6

[a]Taken, with modifications, from Ref. 264.

Three different gas-ionization methods are presented in various compilations of analytical procedures. The methods are (1) the double-standard interpolative method (or, simply, the double-standard method), (2) the single-standard method, and (3) the absolute method (Refs. 10 and 265). Two of these (the double- and single-standard) are discussed by Cameron and Stevens (Ref. 264) and are incorporated in recommended or standard procedures (Refs. 153, 266, and 267).

For all three methods, samples (and standards, if used) are converted to UF_6 if necessary. The UF_6 gas is admitted to the ionizing source of the mass spectrometer through an adjustable leak. The ions that are produced in the source are accelerated through a magnetic field, where they are separated by their mass into monoisotopic ion beams. By varying the magnetic field, each ion beam can be selectively introduced through a slit onto a receiver plate, where it produces a current in proportion to its strength. The voltage produced by the ion currents in the electrometer grid resistor is detected as a peak (isotope) by the peak reader. The relative abundances of the isotopes are calculated from the peak data.

Double-Standard Interpolative Method (Refs. 10, 153, and 264 through 267)

This method, as usually described, is specific for the direct determination of the ^{235}U concentration of UF_6 samples having a ^{235}U content of 60 mole % or less. However, the method is equally appropriate for the direct determination of any of the isotopes in U of any enrichment when suitable UF_6 isotopic standards are available. The method is designed to minimize all known sources of analytical bias.

The unknown sample and two standards whose ^{235}U contents bracket that of the unknown are introduced in sequence into the mass spectrometer, and measurements are made that are a function of the mole ratio of ^{235}U to the total of the other U isotopes. These measurements, together with the known composition of the standards, permit calculation of the ^{235}U composition of the sample by linear interpolation.

The symmetrical, six-entry sequence of sample-standard introduction is designed to minimize biases resulting from instrument drift, sample interaction or memory, and the nonlinearity of the relationship between the measured resistance ratios and the true sample mole ratios. Corrections generally are not required for instrument memory.

Single-Standard Method (Refs. 10, 153, 264 through 267)

This method is applicable to the determination of the isotopic relation between two UF_6 samples. If the abundance of a specific isotope of one sample (the standard) is known, its abundance in the other can be determined. The method is flexible in that the number of times a given material is admitted to the ion source may be adjusted to the minimum required for a specified precision level.

The method may be used for the entire range of ^{235}U isotopic concentrations for which standards are available, and it is adaptable to the determination of any U isotope.

The sensitivity with which differences between two materials can be detected depends on the measuring system used, but ratio-measuring devices can generally read ratio-of-mole-ratio differences as small as 0.0001.

The unknown sample and a standard whose isotopic composition is close to that of the sample are introduced in sequence into the mass spectrometer, and the UF_5^+ ions of the isotopes are focused through a mass-resolving collector slit. For ^{235}U concentrations below about 70 mole percent (the exact concentration depends on the relation of the input resistances for the low- and high-current preamplifiers), measurements are made that are proportional to the ratio of ^{235}U to the total of the other isotopes. These measurements, with the known composition of the standard, permit calculation of the ^{235}U concentration in the sample.

For ^{235}U concentrations greater than about 70 mole percent, measurements are made that are proportional to the ratio of ^{238}U to the total of the other isotopes. The ^{234}U and ^{236}U isotopes are determined independently, and ^{235}U is calculated by difference. Memory corrections are applied, based on the periodic measurement of the ratio of two standards.

Absolute Method (Refs. 10 and 265)

This method is applicable to the determination of the isotopic concentrations of two components (e.g., ^{238}U and ^{235}U) and multicomponents (e.g., ^{238}U, ^{236}U, ^{235}U, and ^{234}U) using a single mass spectrometer. The method is primarily applicable to materials having concentrations of ^{235}U greater than 70 weight percent. Although the method can be used as an absolute method, it is strongly recommended that reference (control) standards be analyzed each day to ascertain the precision and accuracy of the instruments(s) and to provide a basis for bias corrections of the measurement results.

Scope of Applications

The gas-ionization methods may be applied to a variety of chemical and physical forms of U other than UF_6. Chemical treatment is required to convert other compounds to high-purity UF_6 prior to the analysis. For this reason, and because the gas methods require relatively large samples and are troubled by a large memory effect, the methods are usually applied only to UF_6 analysis. The only pretreatment required for UF_6 is purification to eliminate hydrocarbons and hydrofluoric acid. However, considerable care must be taken to ensure a representative sample. Detailed procedures for sampling and/or subsampling are found in References 10, 153, and 265 through 268.

The particular method to be used is dependent on the determination desired and, to some extent, the preference of the facility. The double-standard and single-standard techniques are principally applied to the determination of ^{235}U, although they can be used, with suitable standards, for the determination of other isotopes. The absolute technique is particularly adapted to the determination of two or more isotopes with a single spectrum scan.

The double-standard technique permits direct determination of a single isotope through the measured mole ratio of the isotope to the bracketing enrichment standards. The single-standard technique uses the isotopic relation between the sample and a suitable standard to determine the abundance of the isotope of interest. At high enrichments (greater than about 70 mole percent), the determination of ^{235}U abundance is obtained by difference. In the absolute technique, the ion spectrum is magnetically scanned, and the peak (isotope) data are used to calculate the various isotopic abundances.

Summary of Performance

Table 4.29 summarizes the performance of the method as applied to different materials of different enrichments. Additional method details are presented later in this section. These discussions will correspond respectively to the literature, user and exchange program source categories listed in Table 4.29.

Table 4.29 Summary of performance: gas-ionization mass spectrometric determination of uranium-235

Application	% ^{235}U	Method	Random Error (% RSD)	Source[a]
LEU material	2	Double standard	0.014	L
	1.5	Single standard	0.039	L
	1 to 5	Single standard	0.1	L
	2.01	Absolute	0.25	L
HEU material	92	Double standard	0.028	L
	90.1	Single standard	0.17	L
	93	Single standard	0.02	L
	92.19	Absolute	0.011	L
	93.169	Absolute	0.03	L
UF$_6$	0.7	—	0.027 (0.014 to 0.075)	E
		Single standard	0.015	U
	1.7	—	0.044 (0.015 to 0.083)	E
	3.1	Single standard	0.012	U
	0.3 to 98	Double standard	0.14 to 0.005	U
UO$_2$ powder	2.5 to 3	—	0.039	E
UNH solution	3	—	0.028	E

[a] E = survey of exchange programs; L = literature survey; U = users' survey of production facilities.

Equipment

Although the mass spectrometers used for the various methods are similar, there are some procedure-dependent specifications. For this reason, the instrument specifications are listed by method. They were taken from the indicated references.

Double-Standard Interpolative Method (Refs. 10, 153, and 264 through 267)

A mass spectrometer is required with the following features and capabilities:

1. The instrument must have an electron bombardment ion source having an efficiency such that a sample flow rate of about 0.03 standard milliliters of UF_6 per hour will result in a total ion current for UF_5^+ ions of approximately 10^{-9} A.
2. The sample inlet system must have a minimum of three points for attachment of samples, the necessary valves to evacuate the sample lines and admit the UF_6 into the ion source, and a variable leak to control the flow of UF_6 into the ion source.
3. A dual ion collector must be used. The first detector, called the high-current collector, contains a central slit, preferably adjustable, to permit passage of 95% to 100% of the ions of the ^{235}U isotope (mass 330). This detector intercepts ions of the other U isotopes within a mass range of about 1.5% of mass 330. The ^{235}U ions passing through the slit are intercepted by a second detector, called the low-current collector.
4. The measuring system must provide a precise null-balance measurement of the ratio of the ion signals from the low- and high-current detectors. Such a system usually consists of two electrometer amplifiers, a constant impedance ratio decade, a ratio recorder or two amplifiers, and a digital ratiometer. The sensitivity of the system should be such that a change of 1×10^{-15} A ion current can be detected. An attenuation range of at least a factor of 100 should be provided for the low-current amplifier. If ^{235}U concentrations greater than 60 mole percent are to be determined directly, a switch must be provided to reverse the amplifier leads to the ratio decade panel, and a similar attenuation range must be provided for the high-current amplifier. For those measurements, the ^{235}U still passes through the slit, but the measurement is now a function of the ratio of the other isotopes to the ^{235}U isotope.
5. The resolving power of the instrument should be such that the $^{235}UF_5^+ - {}^{238}UF_5^+$ valley height should be less than 3.0% of the $^{235}UF_5^+$ peak height after the peak height has been normalized. The normalization consists of dividing the observed peak height by the sample ^{235}U concentration, expressed as a percent. This resolution requirement should be met with the collector slit width adjusted to pass at least 95% of the ^{235}U ion beam.
6. If the concentrations of the minor isotopes ^{234}U and ^{236}U are to be measured, the $^{234}UF_5^+ - {}^{235}UF_5^+$ valley should be less than 50% of the $^{234}UF_5^+$ peak height. To meet this requirement it will be necessary to narrow the collector slit width and reduce the ion beam transmission to 70% to 80%.

Single-Standard Method (Refs. 10, 153, 264 through 267)

A single-focusing spectrometer with a 5-in. minimum deflection radius is satisfactory when equipped and focused as follows:

(1) A dual collector is used so that ions from one isotope are passed through a resolving slit and focused on a low-current collector, and ions from all other isotopes are focused on a high-current collector. A resolving slit of adjustable width facilitates measurements of all isotopes.

(2) The measuring circuit provides a precise null-balance measurement of the ratio of the two ion currents. By the use of a voltage divider or decade resistors, ratio recorders, or ratiometers, the portion of the signal on the high-current collector that equals the signal on the low-current collector can be determined. A high-current ion beam of 10^{-10} to 10^{-9} A is necesary, with a signal-to-noise ratio greater than 3000 in the low-current amplifier system.

(3) The instrument is focused for resolution consistent with precision and accuracy requirements. Slit widths, or the percent of the designated ions that will pass through the collector slit, must be specified. Normally, the collector slit is adjusted to transmit at least 95% of an ion beam. Under this condition, the valley between the $^{235}UF_5{}^+$ ion peak and the $^{238}UF_5{}^+$ ion peak should be less than 3.5% of the height of the smaller peak. When minor isotopes ^{234}U and ^{236}U are measured, the interpeak valleys between the ^{235}U and minor isotope peaks must be less than 60% of the minor isotope peaks; the collector resolving slit must be narrowed to reduce beam transmission to 75% for these measurements.

(4) The sample inlet system has two sample holders to which UF_6 containers can be attached. A single, adjustable leak for admitting the sample into the spectrometer ion source is preferred. The manifold should be nickel or Monel and have minimum volume.

(5) The pumping system of the spectrometer analyzer tube must maintain a pressure less than 5×10^{-8} torr with sample flowing into the ion source.

(6) The memory of the spectrometer must be consistent with the accuracy and precision required, since a high memory level is usually more variable than a low one. Memory values of 2% to 3% are typical, but up to 10% memory can be tolerated. The memory characteristics of a spectrometer must be established from periodic measurement of the effect, and usually apply until the ion source is replaced, repairs are made on the sample inlet system, or the instrument is refocused so the rate of flow of UF_6 is altered significantly.

Absolute Method (Refs. 10 and 265)

A single-focusing spectrometer with a 5-in. minimum deflection radius is satisfactory when the following specifications are met:

(1) The mass spectrometer must be capable of resolving at 329, 330, and 331 mass positions so that the valley between the peaks is 10% or less of the height of the 329 or 331 peaks.

(2) The instrument must be equipped with a pumping system that can maintain a pressure of 1×10^{-7} torr or less and 3×10^{-7} torr or less with the sample flowing into the source. Mercury diffusion pumps are preferred for UF_6 work because of their low background at the mass 330 range. Liquid-nitrogen refrigeration is required on the traps to attain the required pressure for proper operation.

(3) The sample-introduction system must have a vacuum manifold with several connections, generally three, for attaching sample tubes. The entire system must be as small as possible to minimize surfaces in contact with the gas, thus reducing the amount of sample required and the sample memory. It must be constructed from materials that are resistant to the corrosive UF_6 gas, such as Ni, Monel, and Cu. The sample is admitted to the mass spectrometer through an adjustable nonfractionating leak. Generally, a liquid-nitrogen trap and a mechanical pump are all that are necessary to maintain a proper sample system vacuum. A mercury diffusion pump is optional.

(4) An electron-bombardment-type ion source is used for UF_6 analysis. The source must be constructed of nonmagnetic materials that are resistant to UF_6, such as Nichrome V or copper, and must be designed so that it may be disassembled for cleaning. The filament from which the 75-V electrons for bombardment are produced is usually constructed of tungsten ribbon or wire. In the sector instrument, a small source magnet of approximately 110 G is used to collimate the beam of the ionizing electrons in the source. The minimum accelerating voltage should be about 1800 V.

(5) The electronics required are those generally found on any gas mass spectrometer. The regulation of the electronic supplies should be about 1 part in 20,000 for both the accelerating voltage supply and the magnet supply. An emission regulator is required also for operating the ionizing filament.

(6) A dual collector consisting of a "high-current" collector plate with an adjustable resolving slit and a "low-current" collector plate is required. Magnetic scanning, either automatic or manual, is used to focus each ion peak through the slit of the high-current

collector plate onto the low-current collector plate. An electrometer capable of measuring ion currents of the order of 1 × 10^{-15} to 1 × 10^{-10} A is required for the low-current collector plate. It is desirable to have a means for measuring and reading the total ion current from the high-current collector plate. A vibrating reed electrometer has been used successfully for both purposes. A method for reading the peaks must be provided, such as a 12-in. strip-chart recorder, galvanometer, and precision potentiometer (or a digital voltmeter).

Additional Apparatus

If samples and standards that are not UF_6 are to be analyzed, conversion equipment will be required. The equipment and procedures presented in Reference 10 are recommended.

Major Sources of Error

Errors most commonly encountered result from the following:

(1) Nonrepresentative sample and/or subsample
(2) Inadequate purification of the sample and standards
(3) Different treatment of sample and standards during preparation and analysis
(4) Operator error, such as—
    (*a*) Mistakes in operation of inlet-system valves that lead to mixing of samples and standards
    (*b*) Improper focusing of the ion beam
    (*c*) Timing inaccuracies in the introduction period of the sample and standards (double-standard method)

The memory effect is the primary interference in the gas-ionization method (Ref. 264). In the UF_6 mass spectrometer, memory occurs both in the sample handling system and in the ion source itself. UF_6 is a vigorous fluorinating agent. It will deposit a layer of UF_4, or other fluorine-containing compounds, on a clean metal surface until the surface has become "conditioned." This conditioned surface will undergo isotopic exchange when reexposed to UF_6. If the isotopic composition of the U of this new UF_6 differs from that of the conditioned surface, an error will result in the isotopic analysis of the new material.

The effect of memory in the sample system can, by proper design and material selection, be made a minor part of the overall effect. Thus, the major component of the memory effect occurs beyond the gas leak in the entrance to the ionization region and in the source itself, where the amount of gas is small compared to the exposed surface and where the exchange becomes significant (Ref. 264). Memory effect corrections are incorporated in both the single-standard and the absolute method either specifically as a "memory correction" or as a "bias correction." Although the double-standard method inherently corrects for this effect, it is recommended that the instrument be conditioned for about 1 h before analysis of samples the isotopic concentration of which is more than 30% different from previously determined samples. The low standard is used for the conditioning.

Significant errors may be introduced into the results unless great care is taken to prevent cross-contamination during any chemical pretreatment and preparation. This is, of course, more of a problem when the sample and/or standard materials are not initially UF_6. Care must also be exercised to avoid mixups when placing the sample and standard(s) (single- and double-standard methods) in the sample-introduction system. Since U can be a common environmental contaminant in nuclear laboratories, scrupulous housekeeping in the working areas is absolutely essential.

Measurement Control Requirements

For the double- and single-standard methods, it is recommended that an NBS or NBL primary U standard of appropriate enrichment be analyzed once per shift. Control charts for the average value for each isotopic ratio should be established. In addition, it is suggested that control charts be established based on the ratios obtained for each reference standard during routine analysis. When the average value for the primary standard ^{235}U mole ratio changes at the 0.05 significance level, the cause(s) for the shifts should be investigated before continuing with the analysis of samples. It is recommended that a second primary standard be run immediately after an "out-of-limit" situation arises to eliminate operator error as a possible cause for the problem. The reference standard control charts can be used to signal an "out-of-limit" situation during the course of the shift.

For the absolute method, two analyses of a primary standard are recommended at the beginning of the shift and after every fifth unknown sample. The average results obtained on the standards are used as a bias correction for the unknown samples. Control charts based on the bias correction values from each primary standard should be established. The control chart data should be used to detect "out-of-limit" situations.

Data Analysis Requirements

The methods used for calculating isotopic composition vary according to the analytical procedure used and according to the isotopic levels encountered and to the standards availability. The calculations are not particularly complex but are diverse and lengthy, and would be performed most effectively on a computer. A detailed description of the calculations required for the specific procedures is too cumbersome to include in this section but may be found in References 10 and 153.

Survey of Selected Literature

The double-standard method shows relative standard deviations (Ref. 153) that range from 0.01% for standards differing by 5% to 0.025% for standards differing by 45%. Results from an interlaboratory evaluation (Ref. 152) showed a bias of −0.02% ± 0.03% and a relative standard deviation of 0.014% at the 2 weight percent ^{235}U level. At the 92 weight percent ^{235}U level, the bias was 0% ± 0.7%, and the relative standard deviation was 0.028%.

The precision of the single-standard method is strongly dependent on the range of concentrations assigned to a given instrument. With instruments that are assigned samples between 1 and 5 weight percent ^{235}U, a relative standard deviation of 0.1% was obtained over a period of 1 yr at two laboratories (Ref. 153). With instruments assigned a range of 93 to 93.5 weight percent ^{235}U, a relative standard deviation of 0.02% was obtained (Ref. 153). In an interlaboratory evaluation of the single-standard method (Ref. 152), relative standard deviations of 0.039% at the 1.50 weight percent ^{235}U level and 0.17% at the 90.10 weight percent ^{235}U level were obtained. The precision of the analysis of 90.10 weight percent ^{235}U is outside the range normally found for this method.

For the absolute method, relative standard deviations (Ref. 265) for replicate measurements of a single standard are 1.8% for ^{234}U (1.005 weight percent), 0.03% for ^{235}U (93.169 weight percent), and 5.9% for ^{236}U (0.323 weight percent). An interlaboratory evaluation (Ref. 152) yielded relative standard deviations ranging from 8.3% to 0.19% for ^{234}U concentrations ranging from 0.012 to 0.97 weight percent, 0.25% to 0.011% for ^{235}U concentrations ranging from 2.01 to 92.19 weight percent, 7.6% to 1.3% for ^{236}U concentrations ranging from 0.014 to 0.25 weight percent, and 0.0044% to 0.17% for ^{238}U concentrations ranging from 97.96 to 6.58 weight percent.

Survey of Production Facilities

Gas-ionization methods are employed at the enrichment facilities to determine the isotopic composition of U in UF_6. The single-standard and double-standard interpolative methods, as described in the previous Sections, are used almost exclusively for determining all levels of ^{235}U concentrations. The single-standard method is used primarily for depleted or low enriched materials and where standards are available that closely approximate the level of the sample. For the single-standard method relative standard deviations of 0.012% and 0.015% were obtained for ^{235}U concentrations of 3.1% and 0.7%, respectively. For the double-standard method relative standard deviations ranged between 0.005% and 0.14% for ^{235}U concentrations between 98% and 0.3%.

Survey of Exchange Programs

Figure 4.11 presents the performance of the gas-ionization method as applied to natural and low-enriched UF_6 by the GAE (Ref. 155) program laboratories. The unweighted average random error for seven laboratories on the 0.7% ^{235}U material is 0.027% RSD. The average for the 1.7% material is 0.044% RSD (5 laboratories).

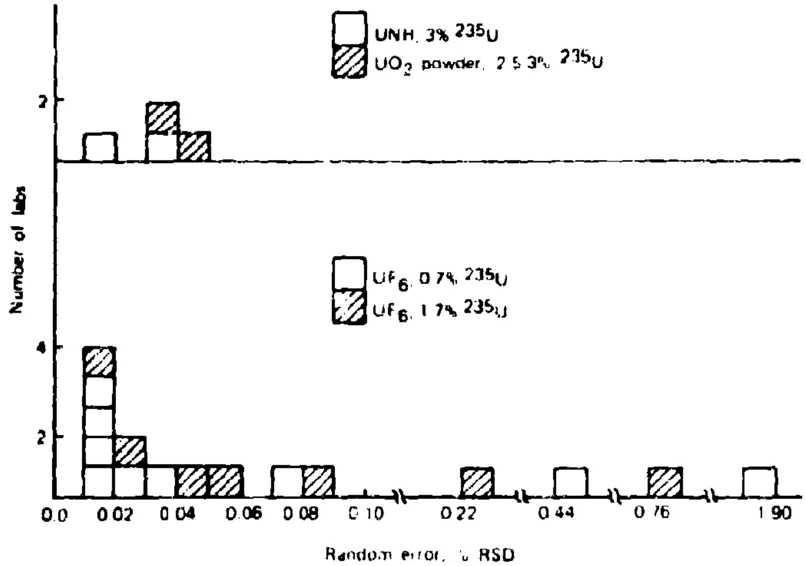

Figure 4.11 Gas-ionization mass spectrometry—exchange program performance.

Method performance as applied to UO_2 powder and UNH solution by the SALE (Ref. 154) program participants is also presented in Figure 4.11. These materials, nominally 3% ^{235}U, require a preliminary conversion to UF_6.

Detailed method descriptions were not available from either of the exchange program reports.

4.9 DETERMINATION OF PLUTONIUM CONCENTRATION

4.9.1 Gravimetry: The Ignition Impurity-Correction Method

Description of Method

The gravimetric determination of Pu as PuO_2 by ignition at 1200°C or higher shares the disadvantages of the gravimetric determination of U and possesses some of its own. From a safeguards point of view, the objection can be raised that the method is nonspecific for Pu. As with the gravimetric method for U, it is applicable only to high-purity compounds, such as product material. The final weight of PuO_2 must be corrected for the nonvolatile impurities as determined by separate analysis. There has also been some controversy concerning the ignition temperature and time required to obtain stoichiometric PuO_2. Other disadvantages involve the handling difficulties associated with Pu-containing powders and the difficulty of dissolving the high-fired plutonium oxide for recovery purposes.

The gravimetric method also has some advantages. High precision is easily attained on a routine basis when rigidly controlled conditions of ignition and regular periodic checks of performance are maintained. Other advantages are that actual operator time per determination is low, only simple laboratory equipment is required, and solid samples do not require dissolution.

For the gravimetric method to produce accurate results, the final weighing form (PuO_2) must have a stoichiometry that is well known and reproducible with high precision. The conditions of ignition under which stoichiometric PuO_2 is formed have been the subject of disagreement. Drummond and Welch (Ref. 269) reported that oxide ignited at 1180°C was nearly stoichiometric ($PuO_{2.002}$). They also found that the oxide would approach constant weight on continued heating at any given temperature between 900°C and 1200°C, but had an oxygen/plutonium ratio greater than 2.000. Oxide calcined at 870°C was found to be hygroscopic in an uncontrolled atmosphere, but oxide calcined at 1200°C was not hygroscopic. Waterbury, Douglass, and Metz (Ref. 270) studied the thermogravimetric behavior of Pu metal, nitrate, sulfate, and oxalate, using larger samples than those used by Drummond and Welch. They observed that the final dioxide from all samples except the nitrate contained excess oxygen after 4 h at 1250°C, indicating that a higher temperature is required to form the stoichiometric dioxide by ignition of these materials in air. The ignition products of the nitrate had an oxygen/plutonium atom ratio of 1.999.

McGowan, Johnson, and Swinburn (Ref. 271) studied gravimetric methods for determining the oxygen/metal ratios in Pu/U oxide fuels. They concluded that oxide produced via the thermal decomposition of Pu(IV) oxalate and ignited at 1250°C in air gave an oxide with an oxygen/plutonium atom ratio of 1.997. Plutonium dioxide prepared in this manner has been used as a chemical reference standard for Pu (Ref. 49).

Lindner and von Baeckmann (Refs. 272 and 273) recommend the gravimetric method for routine use in verifying titrimetric measurements and for giving an upper limit for the Pu content. Since their report may not be readily accessible, their procedure is included:

1) Weigh 500 to 600 mg of PuO_2 into a previously ignited porcelain crucible. (Note: the material is hygroscopic and should be weighed in a dry atmosphere. For requirements, see Ref. 41, p. 3–3.)
(2) Ignite at 1200°C in a muffle furnace for 1 to 2 h.
(3) Allow to cool in desiccator and reweigh.

Scope of Applications

The gravimetric method is applicable to the determination of Pu in pure materials, such as plutonium oxalate, plutonium oxide, plutonium metal, and plutonium nitrate solutions. The method has been applied principally to low-fired plutonium oxide produced by the thermal decomposition of plutonium oxalate.

Summary of Performance

A relative standard deviation of 0.05% to 0.2% for the method has been cited by von Baeckmann (Ref. 273). On 51 sets of determinations in duplicate or higher replication, using plutonium oxalate that had been dried at 400°C, a relative standard deviation of 0.07% was obtained (Ref. 272). Due to trace impurities in the oxalate, the results were 0.1% to 0.2% higher than values obtained by wet chemical analysis. The gravimetric method is thus not an accurate and specific method for the determination of Pu, but gives the upper limit of the Pu contents.

Equipment

(1) Balance: analytical; single pan; capacity of 150 to 200 g; 0.1 mg sensitivity, readability, and precision.
(2) Furnace: muffle, capable of controlled temperatures in the range of 1200°C to 1250°C. A commercially available box furnace with 1500°C maximum operating temperature and control console sold for about $3200 in 1979.
(3) Glovebox: fully enclosed, with dynamic atmosphere of dry nitrogen or air with a dewpoint not greater than −23°C, for handling, sampling, and weighing PuO_2 powder.

Major Sources of Error

Nonvolatile impurities must be separately determined and a correction applied to the weight of PuO_2 obtained in the gravimetric determination. A carrier-distillation spectrometric method is recommended. (See Refs. 63 and 41, p. 6–1.) Concentrations of impurities should preferably not total more than 500 μg/g for accurate results. Iron, which is a common impurity in Pu compounds, may be determined spectrophotometrically. (See Ref. 41, p. 6–22.)

Measurement Control Requirements

The performance of the direct ignition gravimetric method should be checked periodically by use of a precise titrimetric method. For this purpose, the PuO_2 that has been ignited at 1200°C to 1250°C may be dissolved in a mixture of $12M$ hydrochloric acid and $0.1M$ hydrofluoric acid in a Teflon beaker (Ref. 49).

Data Analysis Requirements

Calculate the number of grams of Pu per gram of sample using the following equation:

$$\mathrm{Pu}_A = \frac{W(1 - C)G}{S} \tag{4–34}$$

where

Pu_A = Pu assay, grams of Pu per gram of sample
W = weight of ignited oxide (sum of Pu and impurity oxides), g
C = sum of the weights of impurity oxides found by spectrometric analysis, grams per gram of total ignited oxide
S = weight of sample taken for analysis, g
G = gravimetric factor (Pu/PuO_2) corrected for isotopic composition, grams Pu per gram PuO_2

Survey of Selected Literature

See "Summary of Performance."

Survey of Production Facilities

No routine data were available.

Survey of Exchange Programs

This method was not evaluated by these programs.

4.9.2 Redox Titrimetry

Description of Method

Uranium and plutonium can be determined by titrimetric methods based on oxidation-reduction (redox) reactions. Such methods are probably the most precise and accurate methods available for nonirradiated materials and generally use electrometric end point detection. Methods developed before 1962 were reviewed by Metz and Waterbury (Ref. 7). A review (Ref. 274) by those authors was published in 1959. Sorantin (Ref. 275) included electrometric methods in his review of analytical procedures for Pu and U in nuclear fuels. Milner, Phillips, and Fudge (Ref. 70) recommended several electrometric procedures for the determination of Ce, Ru, Cr, and Fe as well as Pu and U in ceramic nuclear fuel materials. More recently Hakkila (Ref. 76) has reviewed a variety of analytical procedures, including electrometric titrations, for use in the Th-U fuel cycle.

Titrimetric redox procedures are categorized by the method used for detection of the end point. For the purpose of this chapter, these methods are either potentiometric, amperometric, or spectrophotometric. All of these methods are capable of providing relative standard deviations of less than 0.1%.

In a potentiometric titration, the end point is found by measuring the oxidizing (or reducing) potential of the solution as the titration proceeds. This is accomplished by measuring the voltage developed between two electrodes immersed in the titrated solution. One of the electrodes, designated as the reference electrode, is unaffected by changes in the solution. The other (indicating) electrode is an inert, usually noble-metal electrode that is responsive to the oxidation-reduction potential of the solution. The voltage is measured by means of a high-input-impedance instrument so that negligible current will be drawn from the electrodes or solution. When the potential of the solution is monitored continuously during the addition of the titrant solution, it is found that there is a large change in potential (200 to 400 mV) in the vicinity of the end point. The exact end point can be located by constructing a titration curve of potential versus volume of titrant; by mathematical processing of these data; or, if the change in potential is sharp enough, by titrating and stopping the addition of titrant when the large excursion in potential occurs ("dead-stop" technique). Because the change in potential is the critical measurement, the sharpness of the end point is the limiting factor influencing the accuracy of the potentiometric titration.

In amperometric titrations, the end point is found by measuring the current generated by the reaction of an electroactive species in the solution as the titrant is added. This is accomplished with an indicator-reference electrode pair or a pair of indicator electrodes. In the single-indicator electrode method, a potential is applied to the indicator electrode that will make one species (reactant, titrant, or product) electroactive. The potential is held constant with respect to the reference electrode during the titration, and the current that flows through the system is measured with a precision dc picoammeter as a function of the volume of titrant added. In the dual indicator electrode method, the potential difference between the two electrodes remains constant during the titration and the current changes are, again, measured as a function of the added titrant. The exact end point of the titration can be obtained graphically from a plot of the current versus volume of titrant, by mathematical processing of the data, or by "dead-stop" techniques where the current flow at the end point is zero or close to zero. The exactness with which the end point of the titration can be determined is the limiting factor with regard to the accuracy of amperometric titrations. The potential used in the titration can be selected so that the limiting current for either the reactant, titrant, or product is being measured, depending on which yields the sharpest end point.

More detailed descriptions of the potentiometric and amperometric techniques are presented in References 276 and 277.

Scope of Applications

The potentiometric and amperometric titration methods for the determination of Pu are most commonly used for the analysis of final product materials. Many of the titrimetric methods require relatively large quantities of Pu. However, MacDonald and Savage (Ref. 278) describe an amperometric method for the determination of 5 to 60 mg of Pu in samples of irradiated fuel solutions. Redox titrimetric techniques have been applied to both the sequential determination of Pu and U (Refs. 279 and 280) and the determination of Pu in the presence of U (Refs. 53, 62 and 281).

Redox titrimetric methods for Pu are based on either the Pu(VI)-Pu(IV) couple or the Pu(III)-Pu(IV) couple. In the first case, all of the Pu is oxidized to the hexavalent state by a suitable oxidizing agent, usually AgO or Ce(IV). The Pu(VI) is then titrated with a standard Fe(II) solution. Usually, an excess of Fe(II) is added, and the excess is back-titrated with a standard solution of Ce(IV) or dichromate.

In the second case, all of the Pu is reduced to the trivalent state by a powerful reducing agent. The trivalent Pu is titrated with either Ce(IV) or dichromate.

Summary of Performance

Table 4.30 summarizes the performance of the method as applied to different process and product materials. Each method employs a preliminary oxidation or reduction to the Pu(VI) or Pu(III) oxidation state and then titration to the Pu(IV) oxidation state. The end point is detected amperometrically, potentiometrically, or spectrophotometrically. Method details are presented later in this section in discussions that correspond to the literature, user, and exchange program source categories listed in Table 4.30.

Equipment

The redox titrimetric methods require some special instruments in addition to common laboratory apparatus such as analytical balances, volumetric or weight burets, microburets, and glassware. Commercial titration apparatus is available from several sources. Costs range from $2000 to $100,000, depending on the accessories available and the degree of automation; however, the titrations can be performed with the following minimum additional equipment:

(1) Amperometric end point methods.—The apparatus listed is used in the method of Reference 282:
  (*a*) Precision microammeter or picoammeter
  (*b*) Regulated constant potential supply with precision millivolt meter
(2) Potentiometric end point methods.—The listed apparatus is used in the method of References 283 and 284:
  (*a*) Constant current source
  (*b*) Precision millivolt meter; high-performance pH meter with millivolt indication is adequate

The commonly used method of Caldwell et al. (Ref. 285) employs spectrophometric end point detection and, therefore, requires a simple colorimeter or spectrophotometer in place of the current or potential sensing devices listed previously.

Major Sources of Error

Errors most commonly encountered result from:

(1) Uncertainty in the value of the standards used for titrant standardization
(2) Accuracy uncertainty of the analytical balance
(3) Change in titer of a standard solution
(4) Inadequate operator technique

Interference can be caused by ions that undergo the same set of redox reactions as the Pu ions. Such elements will increase the apparent Pu content of the sample. If the interference is quantitative, as is usual with Fe in procedures using the Pu(III)-Pu(IV) couple, an appropriate correction can be made by determination of the Fe content.

Table 4.30 Summary of performance: determination of plutonium by redox titrimetry

Method	Application	Performance (% RSD)		Source[a]
		Random Error	Systematic Error	
Pu(VI)-Pu(IV) couple:				
Amperometric or potentiometric end point, 4 to 250 mg Pu	Process/product material	0.03 to 0.26	—	L
Amperometric end point	Pu metal	0.038	0.038	U
		0.049	—	E
	PuO_2 powder	0.42[b]	0.038	U
		0.13[b]	0.11	U
		0.059	—	E
	PuO_2 pellets	0.24[b]	0.11	U
	$(Pu,U)O_2$ powder	0.081	—	E
	$(Pu,U)O_2$ pellets	0.62[b]	0.038	U
		0.14, 0.18	—	E
	(Pu,U)C pellets	0.56[b]	0.038	U
	(Pu,Th)C pellets	2.9[b]	0.038	U
	$Pu(SO_4)_2{\cdot}4H_2O$ (NBS 944)	0.36	0.11	U
	$Pu(NO_3)_4$	0.099, 0.24	—	E
Potentiometric end point	PuO_2 powder	0.079, 0.098	—	E
	$Pu(NO_3)_4$	0.23, 0.24	—	E

Note—See footnote at end of table.

Table 4.30 Summary of performance: determination of plutonium by redox titrimetry (Cont'd)

Method	Application	Performance (% RSD) Random Error	Performance (% RSD) Systematic Error	Source[a]
Pu(III)-Pu(IV) couple:				
Potentiometric end point, 25 to 600 mg Pu	Process/product material	0.02 to 0.1	—	L
Potentiometric end point, 4 to 50 mg Pu	Process/product material	0.2 to 2.25	—	L
Spectrophotometric end point (ferroin)	Process/product material	0.07 to 0.14	—	L
	Pu metal	0.086	—	U
		0.021, 0.049	—	E
Potentiometric end point	PuO_2 powder	0.085 to 0.15	—	E
	$(Pu,U)O_2$ powder	0.17, 0.35	—	E
	$Pu(NO_3)_4$	0.12 to 0.22	—	E

[a] E = survey of exchange programs; L = literature survey; U = users' survey of production facilities.

[b] Includes sampling error.

Other elements will tend to give low results, apparently as a result of their being insoluble under the pretreatment conditions of a particular procedure, resulting in a partial removal of Pu by coprecipitation. Diverse ions can also cause interferences by masking or diminishing the sharpness of the end point.

There is conflicting evidence regarding the interference due to americium. Bergstresser and Waterbury (Ref. 35) report that Am present at levels ranging from 0.05% to 0.20% (relative to the Pu content) results in positive errors in the amperometric method of Seils, Meyer, and Larsen (Ref. 282) ranging from 0.06% to 0.11%, respectively. The effect is not directly proportional to the concentration of Am in the Pu sample. Spevackova, Guichard, and Cauchetier (Ref. 286) report that Am present at levels ranging from 2% to 20% of the Pu content causes a nonreproducible interference in methods using argentic oxide oxidation. However, Bartscher, Lefebvre, and Baumann (Ref. 287) have investigated the effect of Am on both Pu(VI)-Pu(IV) and Pu(III)-Pu(IV) methods and report that the methods can tolerate Am to Pu ratios of 1:10.

Measurement Control Requirements

An aliquot of a standard solution prepared from a suitable primary reference material (e.g., NBS 949) should be analyzed at least once a shift. A control chart for the average Pu value should be established. When the value changes at the 0.05 significance level, the redetermination should be performed. If the deviation from the expected value is confirmed, the cause(s) should be investigated and, if necessary, the procedure should be recalibrated.

New chemicals and reagents should be tested to ensure that they do not alter the precision and accuracy of the procedure. It is advisable to recalibrate whenever reagents are replaced with material from a different lot.

Routine checks of the procedure in use for precision and accuracy are recommended.

Data Analysis Requirements

The calculations are method specific. Typical examples are discussed in the following sections.

Amperometric Titration

The calculation presented in Reference 288 for the method of Seils, Meyer, and Larsen (Ref. 282) is typical and is reproduced as originally published for illustrative purposes.

Graphical Method

The end point can be determined graphically by plotting the intersection of the horizontal residual current line and the Fe(II) diffusion current line. The residual current line has a slope of zero and is fixed by the residual current measurement. The Fe(II) diffusion current line is fixed by the second and third current-mass measurement. The plotted data have the configuration of a reversed letter L.

Formula Method

Calculate the grams of Pu per gram of sample by using the following formula:

$$\mathrm{Pu/g} = \frac{(A - B)CD}{M} \qquad (4\text{-}35)$$

where

$\mathrm{Pu/g}$ = grams of Pu per gram of sample
$A - B$ = grams of titrant required by plutonium
= $(a - b) - [(e - d)(b - c)/(f - e)]$
a = first mass of the buret and titrant, g
b = second mass of the buret and titrant, g
c = third mass of the buret and titrant, g
d = first current reading, μA (residual current)
e = second current reading, μA
f = third current reading, μA
C = milliequivalent/gram of Fe(II) titrant
D = milliequivalent mass of plutonium (adjusted for isotopic composition)
M = sample weight, g

Use the appropriate dilution factors and the weight of the sample aliquot to calculate the plutonium content of the original sample.

Potentiometric Titration

The calculation given in Reference 62 is typical of those for the procedures based on the Pu(VI)-Pu(IV) couple, using an excess of Fe(II) reductant:

$$\mathrm{Pu,\ mg} = \frac{(C - B)NV\,(\text{atomic weight Pu}/2)}{A} \qquad (4\text{-}36)$$

where

C = volume of Ce(IV) solution equivalent of total Fe(II) added, mL
B = volume of Ce(IV) solution equivalent of total Fe(II) excess, mL

N = normality of Ce(IV) solution
V = volume of sample solution, mL
A = volume of aliquot taken for analysis, mL

The calculation given in Reference 289 is typical of those for procedures based on the Pu(III)-Pu(IV) couple. The method uses Cu(I) as the reductant and potassium dichromate as the titrant. Two inflection points are obtained in the titration. The first corresponds to the complete oxidation of the excess Cu(I) and the second to the complete oxidation of the Pu(III). The calculation procedure is as follows:

$$\text{Pu, mg/mL} = \frac{F(T - t - B)}{V} \qquad (4\text{–}37)$$

where

F = mg of Pu equivalent to 1 mL of titrant
T = total volume of titrant required to reach the second inflection point, mL
t = volume of titrant required to reach the first inflection point, mL
B = blank titer, mL
V = volume of sample taken, mL

Survey of Selected Literature

Tables 4.31 and 4.32 summarize the more widely used redox titrimetric methods for the determination of Pu in process or product materials. More detailed information is given in the following paragraphs or can be found in the cited references.

Methods Based on the Pu(VI)-Pu(IV) Couple

The amperometric method of Seils, Meyer, and Larsen (Ref. 282) is used routinely for the determination of Pu when the form of the Pu-bearing sample is such that pretreatment can yield a soluble sulfate. The method is, therefore, applicable to Pu in the form of Pu metal, oxide, fluoride, chloride, nitrate, and sulfate, and in alloys containing constituents such as U, Fe, Co, and Al. Samples containing from 10 to 20 mg of Pu yield the maximum precision and accuracy (Ref. 282).

In this method the Pu is oxidized to the hexavalent state in a 0.25M sulfuric acid solution with argentic oxide. After the excess oxidant is destroyed in heating, the Pu is titrated amperometrically with standard Fe(II) sulfate. The end point is detected by measuring the current generated by excess titrant at a rotating platinum microelectrode versus a saturated mercurous sulfate reference electrode.

Table 4.31 Redox methods for determination of plutonium using the Pu(VI)–Pu(IV) couple[a]

Oxidant	Back Reductant	Titrant	End Point	Sample Size (mg)	RSD (%)[b]	Interferences, Comments	Ref.
AgO	Fe(II)	—	Amperometric	10 to 20	0.03	V, Mn, Cr, Ce, Ru, Au, Rh, Pt, Pb, Am, Np. Separation procedure recommended (Ref. 282).	291, 35, 152, 282[c]
AgO	Excess Fe(II)	Ce(IV)	Potentiometric	4	0.1 to 0.19	V, Mn, Cr, Ce, Ru, Au, Rh, Pt, Pb, Am, Np. Separation procedure recommended (Ref. 282).	281, 62[d]
AgO	Excess Fe(II)	$K_2Cr_2O_7$	Potentiometric	20 to 80	0.17 to 0.26	V, Mn, Cr, Ce, Ru, Au, Rh, Pt, Pb, Am, Np. Separation procedure recommended (Ref. 282).	As above.
$HClO_4$	Excess Fe(II)	Ce(IV)	Potentiometric	200 to 250	0.03	Cr, Au, Mn, Pt.	274, 53, 291, 152[e]
AgO	Excess Fe(II)	$K_2Cr_2O_7$	Amperometric	200	0.05	V, Ce, Cr, and Mn. Interference eliminated by selective reduction with As(III) and Os(VIII) catalyst.	293
Ce(IV)	Excess Fe(II)	$K_2Cr_2O_7$	Amperometric	5 to 60	0.1	V. Amperometric or potentiometric end point. Former not affected by fission product simulate. Uses As(III) and Os(VIII) catalyst.	278

[a] After Table XIII, Ref. 7.

[b] Generally, the optimum RSD obtainable for fuel process or product sample.

[c] See also Ref. 10, pp. 254–261, and Ref. 290, Methods C-697 and C-698.

[d] See also Ref. 10, pp. 261–268.

[e] See also Ref. 10, pp. 299–306.

Table 4.32 Redox methods for determination of plutonium using the Pu(III)–Pu(IV) couple[a]

Reductant	Oxidant	End Point	Sample Size (mg)	RSD (%)[b]	Interferences, Comments[c]	Ref.
Zn amalgam	Ce(IV)	Potentiometric	600	0.02 to 0.06	Fe, Mo, Ti, [illegible], W.	294, 291, 152[d]
Jones reductor	$K_2Cr_2O_7$	Potentiometric	250 to 400	0.03 to 0.04	Cr, Fe, Mo, Ti, [illegible] W. Anion exchange separation recommended to remove interferences.	283, 284[e]
Pb or Jones reductor	Ce(IV)	Spectrophotometric (ferroin indicator)	500	0.07 to 0.14	Fe, Ga, Mo, Ti, U, Cr, NO_3.	285, 291, 152[f]
Ti(II)	Ce(IV)	Potentiometric (Ref. 297 visual)	25 to 350	0.07 to 0.1	Cu, Fe, U, W, NO_3.	64, 295, 296, 291, 297[g]
Cr(II)	Ce(IV)	Potentiometric	20 to 50	0.4	Fe, U, Cu, W.	298
Cu(I)	$K_2Cr_2O_7$	Potentiometric	20 to 40	0.4	Tc, I. Procedure modifications for Tc, I, oxalate removal and application to TBP solutions. Useful range: 3 to 50 mg.	289
Cr(II)	$K_2Cr_2O_7$	Potentiometric	4 to 19	2.25 to 0.25	Fe, Cu, V, Pt, Mo, W, NO_3. Sequential determination of U and Pu.	280
Ti(II)	$K_2Cr_2O_7$	Amperometric	8 to 30	1.3 to 0.19[h]	Fe, V.	279

TBP = tributylphosphate

[a] After Table XIV, Ref. 7

[b] Generally, the optimum RSD obtainable for fuel process or product samples.

[c] Generally, Fe interference is quantitative and an appropriate correction can be made.

[d] See also Ref. 10, pp. 274–285.

[e] See also Ref. 10, pp. 285–292.

[f] See also Ref. 10, pp. 268–274.

[g] See also Ref. 10, pp. 293–299 and Ref. 290, Method C-697.

[h] Precision (1σ) (Pu/Pu + U)%.

Iron and uranium do not interfere with the Pu determination. Substances that are oxidized by the argentic oxide and later reduced to a lower oxidation state by ferrous sulfate result in a positive error. Elements producing this type of error include V, Cr, Mn, Ce, Ru, Au, Rh, and Pt (Refs. 35, 282, and 288). Thallium, Se, Ca, Ba, and Pb cause low results, probably because there is a partial coprecipitation of Pu during the formation of an insoluble material when the sample is fumed with sulfuric acid. Americium interference is not quantitative.

Seils, Meyer, and Larsen (Ref. 282) reported a precision of 0.06% RSD for a single determination. The figure was based on 10 titrations of 10 separately weighed portions of a single sample. Each portion contained 10 to 20 mg of Pu. No significant bias was found.

An evaluation of the method at Los Alamos (Ref. 35) gave an RSD for a single determination of 0.03%. This value was obtained by the analysis of high-purity (total impurities less than 0.03%) Pu metal. Over a 10-month period, five portions of the metal were analyzed by sextuplicate determinations of 10 to 20 mg each. No significant bias was found.

The two methods described in References 281 and 62, and Reference 292, are, in essence, modifications of the method just discussed. Both use argentic oxide as an oxidant and Fe(II) as a reductant. Iron(II) is added in excess and back-titrated to a potentiometric end point. The method of References 281 and 62 uses Ce(IV) solution as the back-titrant, while that of Ref. 292 uses potassium dichromate. The normal potentiometric end point with potassium dichromate is poor. This is overcome by using polarized gold electrodes. These methods are in use in Europe and in some U.S. plants.

The method of Waterbury and Metz (Ref. 274) uses perchloric acid to oxidize the Pu, followed by reduction with an excess of Fe(II), and back-titration with Ce(IV). Fewer cations interfere with this method than the argentic oxide procedures, since perchloric acid is a weaker oxidant. However, many plants prohibit the use of perchloric acid, and, as a result, this procedure is not in common use.

The amperometric end point detection method developed by Hedrick et al. (Ref. 293) is a further modification of the procedure of Drummond and Grant (Ref. 292). Interference due to Ce, Cr, and Mn is eliminated by selective reduction prior to titration with arsenite and Os(VIII) catalyst. Excess As(III) is titrated visually with permanganate, and the excess permanganate is destroyed by oxalic acid. Vanadium interference is not eliminated by this technique.

MacDonald and Savage (Ref. 278) have used the ability of As(III) in the presence of Os(VIII) to eliminate Ce(IV) interference to permit the use of Ce(IV) as the initial oxidant. Their method is like the method of Reference 294 with the noted change in the oxidant. It is claimed that the method can be used for solutions containing fission products. However, the required sample size (5 to 60 mg of Pu) strongly suggests that an alternative method that uses smaller samples would be preferable.

Methods Based on the Pu(III)-Pu(IV) Couple

The most commonly used of the procedures based on the Pu(III)-Pu(IV) couple is that developed by Caldwell et al. (Ref. 285) ("Rocky Flats" or "RF" method). The method is applicable to the determination of Pu in the form of metal, in oxides and nitrides, and in various compounds and solutions. The method as described in Reference 285 specifies a 500-mg sample size. However, Waterbury and Metz (Ref. 291) evaluated a modification of the method with samples of 100 to 200 mg with no appreciable loss of precision.

In this method Pu in the dissolved sample is reduced to Pu(III) in a lead reductor or Jones reductor and then is oxidized to Pu(IV) with a standard ceric sulfate solution. The end point is detected spectrophotometrically using ferroin as the indicator. The lead reductor is recommended for solutions prepared from Pu metal to avoid interferences caused by alloying elements (such as gallium) that are not eliminated by the Jones reductor. If a number of potential interferences are present, separation of the Pu by anion-exchange from 8*N* nitric acid solution is recommended (Ref. 285).

In the assay of high-purity Pu metal, Fe is usually the only titratable impurity. In the "Rocky Flats" method, Fe reacts stoichiometrically. A correction can be made by determining Fe in a separate sample aliquot. Generally, an Fe correction can be made in that manner for all procedures based on the Pu(III)-Pu(IV) couple.

Other metals that would be expected to interfere include Cr, Ti, Ga, Mo, W, U, and V. Nitrate ion also interferes through its effect on the preliminary reduction with the lead or Jones reductor.

Over a period of 11 months, 188 samples were resubmitted and analyzed in duplicate. A standard deviation, calculated from the means of the samples and their resubmissions, was 0.05%, corresponding to a standard deviation of 0.07% based on individual samples (Ref. 285). The results from an evaluation by various laboratories (Ref. 152) gave a relative standard deviation of 0.14% for sulfuric acid solutions of plutonium sulfate tetrahydrate and a bias of +0.1% ± 0.3%.

The earliest reported method for the potentiometric determination of Pu used reduction with zinc amalgam in the titration cell and titration with standard ceric sulfate (Ref. 294). The optimum sample size was 600 mg, with interference problems similar to those cited previously. Although the method has a high precision, it is not in general use.

The method of References 283 and 284 uses a Jones reductor with subsequent oxidative titration with potassium dichromate. Polarized gold electrodes are used to overcome the end point definition problem already mentioned. For sample sizes ranging from 250 to 400 mg, RSDs of 0.03% to 0.04% are reported (Refs. 283 and 284). Interferences are similar to those previously cited.

Methods that use reduction with Ti(II) and oxidation with Ce(IV) have been reported and/or evaluated by a number of workers (Refs. 291, 64, and 295 through 297). Results with sample sizes ranging from 25 to 350 mg yielded RSDs of 0.07% to 0.1%. As with most methods based on the Pu(III)-Pu(IV) couple, the interferences are essentially those cited. This method, as well as most of those to be discussed, involves two inflection points (end points). The first corresponds to the complete oxidation of the excess reductant and the second to the completion of oxidation of Pu to the (IV) state. The double end point increases the error resulting from inaccuracies in end point detection.

The method of Reference 298 uses Cr(II) as the reductant and Ce(IV) as the oxidant. Relative standard deviations of 0.4% have been reported for 20- to 50-mg samples. Presumably, increasing the sample size to that used in the methods discussed previously would lower the RSD. The method involves a double end point and has the interferences characteristic of this group of methods.

Davies and Townsend (Ref. 289) report a method using Cu(I) as the reductant and potassium dichromate as the oxidant. The end point is detected potentiometrically, but polarized electrodes are not used. A precision of 0.4% RSD was obtained in the titration of 20 to 40 mg Pu. Two end points must be detected. The method has been applied to aqueous Pu and Pu-U nitrate solutions, TBP-kerosene solutions, and dissolver feed solutions. The method is in use in the United Kingdom and in France.

Two methods have been reported that provide sequential determination of U and Pu (Refs. 279 and 280). The method of Kato and Takahashi (Ref. 280) uses Cr(II) as the reductant and potassium dichromate as the oxidant, with potentiometric detection of the end points. The method has been evaluated for samples containing 3.86 to 19.31 mg of Pu and 46.99 to 18.80 mg of U. The precision obtained for Pu ranged from 2.25% to 0.26% RSD. The reported interferences are Fe, Cu, V, Pu, Mo, W, and nitrate. The method of Chadwick and McGowan (Ref. 279) uses Ti(II) as the reductant and potassium dichromate as the oxidant, with amperometric detection of the end points. Reported interferences are Fe and V; however, other interferences typical for this group of methods are to be expected. For samples containing 8 to 30 mg of Pu, the precision based on Pu/(Pu + U) is reported to be 1.3% to 0.19%.

Survey of Production Facilities

Two facilities have reported routine performance data on methods employing an amperometric end point. The first method, not defined in detail, employs a titration with standard ferrous ammonium sulfate

[Pu(VI)-Pu(IV) couple]. The method was applied to the following materials with the corresponding random errors:

Material	Random Error (% RSD)
Pu metal	0.038
(Pu,U)C pellets	0.56 (Includes sampling error)
(Pu,Th)C pellets	2.9 (Includes sampling error)
$(Pu,U)O_2$ pellets	0.62 (Includes sampling error)
PuO_2 powder	0.42 (Includes sampling error)

A systematic error based on the repetitive measurement of a control standard (NBS 949 Pu metal) of 0.038% RSD was obtained.

In the second method [Pu(VI)-Pu(IV) couple] 10 to 20 mg of Pu is oxidized with AgO and then titrated with ferrous ammonium sulfate. Replicate measurements of plutonium sulfate tetrahydrate (NBS 944), PuO_2 powder, and PuO_2 pellets yielded random errors of 0.36%, 0.13%, and 0.24% RSD respectively. The systematic error of the method is 0.11% RSD and is based on repetitive measurement of the NBS 944 standard, which is no longer available.

A third facility employs a spectrophotometric end point. A sample containing 500 mg Pu is reduced in a lead reductor [Pu(III)-Pu(IV) couple] and titrated with ceric sulfate to the spectrophotometric end point using ferroin as indicator. The random error of the method as applied to Pu metal is 0.086% RSD.

Survey of Exchange Programs

The SALE program (Ref. 154) participants employ five different redox titrimetric methods. Two methods call for a preliminary oxidation with AgO [Pu(VI)-Pu(IV) couple], reduction with excess Fe(II), and titration with Cr(VI) or Ce(IV) to amperometric or potentiometric end points, respectively. The other three methods use the Pu(III)-Pu(IV) couple in which the Pu is reduced with zinc amalgam (Jones), Cu(I), or Ti(III). The Pu(III) is then titrated with standard Cr(VI) or Ce(IV) solution. Method details and performance are presented in Tables 4.33 and 4.34.

Three laboratories in the plutonium metal sample exchange program (R. L. Carpenter, Rocky Flats Plant, unpublished information, Sept. 1979 to June 1980) employ redox titrimetric methods for the determination of Pu in Pu metal. Two laboratories employ lead reduction prior to a Ce(IV) titration to a ferroin photometric end point [Pu(III)-Pu(IV) couple]. Random errors of 0.021% and 0.049% RSD were obtained for the method by the two laboratories. The third laboratory employs a preliminary AgO oxidation followed by a reduction with excess Fe(II) and then titration of the excess Fe(II) with Ce(VI) to an amperometric end point. A random error of 0.049% RSD was obtained for the method.

Table 4.33 Redox titrimetric methods for determination of plutonium—sale exchange program: Pu(VI)–Pu(IV) couple

Oxidant	Reductant	Back Titrant	End Point	Application	Random Error (% RSD)	Comments
AgO	Excess Fe(II)	$K_2Cr_2O_7$	Amperometric	PuO_2 powder	0.059	5 to 10 mg Pu
				$(Pu,U)O_2$ powder	0.081	
				$(Pu,U)O_2$ pellets	0.18	
					0.14	
				$Pu(NO_3)_4$	0.099	
					0.24	
AgO	Excess Fe(II)	Ce(IV)	Potentiometric	PuO_2 powder	0.079	—
					0.098	
				$Pu(NO_3)_4$	0.23	
					0.24	

Table 4.34 Redox titrimetric methods for determination of plutonium—sale exchange program: Pu(III)–Pu(IV) couple

Reductant	Oxidant	End Point	Application	Random Error (% RSD)	Comments
Jones	$K_2Cr_2O_7$	Potentiometric	PuO_2 powder	0.085	—
			$(Pu,U)O_2$ powder	0.17	
			$Pu(NO_3)_4$	0.16	
Excess Cu(I)	$K_2Cr_2O_7$	Potentiometric	PuO_2 powder	0.15	Two potentiometric breaks: excess Cu(I) and Pu(III).
			$(Pu,U)O_2$ powder	0.35	
			$Pu(NO_3)_4$	0.22	
				0.12	
Excess Ti(III)	Ce(IV)	Potentiometric	PuO_2 powder	0.11	Two potentiometric breaks: excess Ti(III) and Pu(III).

4.9.3 Complexometric Methods

Description of Method

Reagents that form stable complexes with Pu can be used in titrimetric analysis if a suitable end point indicator is available. If the reagent either forms or removes a colored complex (or compound), the color change can be used for end point determination. Alternatively, the end point indicator may be a dye that forms a colored complex with a somewhat lower stability constant than the compound being titrated.

The most commonly used complexometric titrant for Pu (as well as Th and U) is the disodium salt of (ethylenedinitrilo) tetraacetic acid (EDTA). Since strong complexes are formed, sharp end points can be obtained. The fact that EDTA forms complexes with many elements is, however, a major drawback to its use. By careful selection of pH and indicator and selectively complexing potential interferences, the problems resulting from the lack of specificity of the reagent can often be overcome. Complexometric titrations, as well as other methods for Th, U, and Pu, have recently been reviewed by Hakkila (Ref. 76).

From the safeguards viewpoint the lack of specificity of the complexometric procedures is a serious problem. For example, if a Th-containing solution is substituted for the Pu sample or is added to a Pu sample, the substitution would not be detected and the analytical result would overstate the Pu content. Because of this, it is strongly recommended that a Pu-specific separation step be added to the procedure to remove such interferences. Alternatively, methods that do not suffer from these interferences can be used.

All oxidation states of Pu form 1:1 complexes with EDTA (Refs. 299, 300, and 301). Potentially, this fact eliminates the need for a valency-conditioning step, provided a suitable end point indicator is available. Brown et al. (Ref. 300) have used copper-1-(2-pyridylazo)-2-naphthol (Cu-PAN) as an indirect indicator for end point detection because it will form colored complexes with cations that do not form such complexes with PAN. However, their sample pretreatment should ensure that all the Pu in the sample is in the same oxidation state. Although Boase, Foreman, and Drummond (Ref. 299) noted that a valency-conditioning step was not required, their procedure incorporates a similar Pu extraction step that requires all Pu to be in the tetravalent state. In general, complexometric titrations involve either trivalent or tetravalent Pu.

Scope of Applications

Complexometric titrations can be applied to most Pu-containing materials that can be put into solution. Interferences must often be removed before titration unless highly pure solutions are analyzed. The large sample sizes required by most methods make them unsuitable for analysis of irradiated fuel dissolver solutions. However, Boase, Foreman, and Drummond (Ref. 299) developed a procedure specifically for that purpose. Most procedures require milligram quantities of Pu.

Summary of Performance

Random errors of 0.4% to 0.6% RSD and relative accuracies of 0.4% to 1.0% have been reported in the literature for the different complexometric titration method variations. Specific method details may be found later in this section and in the cited references. No routine data were available from the user survey of production facilities. This method was not used in the exchange programs.

Equipment

Most of these procedures require standard analytical laboratory apparatus. A simple photometer-titration assembly is required for the method described in Reference 299. Photometric detection of the end point can be applied to any of the methods under discussion.

Major Sources of Error

Sources of error in the complexometric procedures are those common to titrimetric analysis; pipetting and/or weighing errors, end point detection errors, and inadequate pretreatment. Interferences for each method are discussed in "Survey of Selected Literature" and listed in Table 4.35.

Measurement Control Requirements

Aliquots of a standard solution prepared from a primary reference standard, such as NBS 949, should be analyzed at least once per shift. Control charts based on the average values should be established. If a measured value exhibits a change at the 0.05 significance level, a replicate measurement should be made. If the second measurement confirms the observed change, the reason(s) for the change should be investigated and a recalibration should be performed.

Routine checks of accuracy and precision are recommended. The accuracy check can be based on the analysis of the standard solution. Boase, Foreman, and Drummond recommended the use of a Pu standard of similar isotopic composition for maximum accuracy (Ref. 299). Precision checks should be based on replicate analyses of standard samples made over a period of time (several days to 1 week). The procedure should be restandardized whenever reagents are replenished.

Table 4.35 Complexometric titration methods for plutonium

Complexing Agent	Back Titrant	End Point Indicator	Separation Technique	Sample Size	RSD (%)	Interferences, Comments	Ref.
EDTA (acetone solution)	$ZnCl_2$ solution	Dithizone, photometric	Hyamine 1622[a] in benzene	100 μg	0.4	Interferences removed by separation step.	299
EDTA (pH: 2.5 to 3.0)	Direct method[b]	Cu-PAN,[c] visual	Suggested to eliminate interferences	14 mg	0.6	Ni, Fe(III), Ce(III), Ce(IV), Cr(III), Al, Cu(II), Bi(III), Au(III), Co(II), Cd(II), Mn(II), Zn, Th.	300
EDTA (pH: 2.5 to 3.0)	Indirect method,[b] $Cu(NO_3)_2$	PAN, visual	Suggested to eliminate interferences	14 mg	0.6	Ce(III), Ce(IV), Co(III), Au(III), Co(II), Zn, Th.	300
EDTA (pH: 2.5)	Thorium nitrate solution	Alizarin red S and methylene blue, visual	—	9 to 15 mg	1.0[d]	Suggested Fe, Ti, Th, Ga, V, but did not test. Some interference from plutonium-chloride complex. End point sensitive to age of plutonium solution.	302
EDTA (0.1 to 0.2*N* HNO_3)	Direct method	Arsenazo-I, visual	—	2 to 20 mg	0.4[d]	Fe(III), Th.	303
DTPA (0.3 to 0.4*N* HNO_3)	Direct method	Xylenol orange, visual	—	239 to 717 μg	1.0[d]	Fe(III), Hg(II), Zr. Method also used for determination of Th, U(IV), and Np(IV).	185

[a] For identification, see text.

[b] See text for description of direct/indirect methods

[c] Xylenol orange found equivalent to Cu-PAN.

[d] Error (relative accuracy).

EDTA = (ethylenedinitrilo) tetraacetic acid; PAN = 1-(2-pyridylazo)-2-naphthol; DTPA = diethylenetriamine pentaacetic acid.

Data Analysis Requirements

The calculation of the Pu concentration is dependent on the particular method being used. A correction for the reagent blank will be required. The following calculation for the method presented in Reference 299 is fairly typical:

$$C = 1000 \frac{W(V_2 - V_1)M}{V_a} \tag{4-38}$$

where

C = concentration of Pu, μg/mL
W = atomic weight of Pu, g/mole
V_2 = sample titer, mL
V_1 = blank titer, mL
M = molarity of the titrant solution, moles/L
V_a = volume of initial sample aliquot, mL

Survey of Selected Literature

A summary of the following complexometric titration methods is presented in Table 4.35.

Milner and Woodhead (Ref. 302) describe an EDTA method for Pu(III) based on back-titration with thorium nitrate at pH 2.5 in hydrochloric acid medium to an alizarin red S-methylene blue end point. The addition of the methylene blue was found to overcome the slight difficulties resulting from the inherent blue color of Pu(III) ions by shifting the end point color from green to purple. The method was tested with Pu solutions freshly prepared by dissolving Pu metal in hydrochloric acid. With amounts of Pu between 9 and 15 mg, relative accuracies of better than 1% were obtained. With amounts in excess of 15 mg, the end point sharpness deteriorated with resultant loss of accuracy. For amounts ranging from 2 to 9 mg of Pu, the accuracy is also decreased. No precision data are given. The authors indicate expected interferences from Fe, Ti, Th, Ga, and V, but did not evaluate the effect of those cations experimentally.

Palei and Chang (Ref. 303) described a direct EDTA titration method for Pu(IV) using arsenazo-I as the end point indicator. The titration is performed in 0.1 to 0.2*N* nitric acid, with the end point indicated by a color change from blue-violet to rose. The low acidity of the solution eliminates many possible interferences. Ferric ion interferes strongly and cannot be tolerated in amounts greater than 3% to 4% of the Pu content. La(III), Cr(III), Pb(II), and Ni(II) do not interfere. Uranyl ions can be tolerated in amounts that are 140 times the Pu content. The authors indicate that interferences from Th, Zr, and U(IV) can be expected even at low concentrations but present no data to confirm this statement. The average error (relative accuracy) reported for the recommended procedure is 0.4%.

Brown et al. (Ref. 300) developed a direct and an indirect EDTA titration method. In the direct procedure, a solution containing 8 to 40 mg of Pu is buffered between pH 2.5 and 3.0, heated to boiling, and titrated with EDTA to a Cu-PAN end point. The indirect procedure is a continuation of the direct procedure. Buffered ammonium fluoride solution is used to stoichiometrically demask the EDTA from the Pu complex. The uncomplexed EDTA is titrated with standard Cu solution to a PAN end point. Considerable care must be taken with the direct titration as the end point is approached. The authors recommend waiting 1 min. between additions of EDTA.

Fourteen cations interfere with the direct titration: Ni(II), Fe(III), Ce(III), Ce(IV), Cr(III), Al(III), Cu(II), Bi(III), Au(III), Co(II), Cd(II), Mn(II), Zn(II), and Th(IV). Seven of these also interfere with the indirect method: Ce(III), Ce(IV), Al(III), Au(III), Co(II), Zn(II), and Th(IV). Phosphate ions interfere through precipitation of Pu. Separation of Pu from interfering ions prior to the conversion to Pu sulfate is recommended. In the absence of interferences the relative standard deviation of both the direct and indirect titration is 0.6% at the 14 mg level.

Boase, Foreman, and Drummond (Ref. 299) describe a method that is applicable to irradiated fuel dissolver solutions. Pu(IV) is extracted using a quaternary amine, Hyamine 1622, dissolved in benzene. The benzene is removed by evaporation and the residue is dissolved in acetone. An excess of EDTA is added and the residual uncomplexed reagent is back-titrated to a dithizone end point with standard zinc chloride solution. The end point is detected photometrically. Hyamine 1622 is essentially *p*-di-isobutylphenoxyethoxyethylbenzyldimethylammonium chloride. The method has a relative standard deviation of 0.3% to 0.4% and an accuracy of about 0.3% at the 100-μg Pu level. Neptunium will interfere but the resulting bias is much less than 1%. The bias can be eliminated by analysis of a Pu standard spiked with Np, or by use of a correction curve of Np concentration versus irradiation level. Ce(IV) destroys dithizone but is reduced to Ce(III) by the Fe(II) conditioner used in the extraction step. Uranium does not interfere.

Rykov, Piskunov, and Timofeev (Ref. 185) describe a method for determining Th(IV), U(IV), and Np(IV) as well as Pu(IV) by direct titration with DTPA using xylenol orange as the end point indicator. Each of the elements may be expected to interfere with the determination of the other, if present in the tetravalent state. Interferences from Fe(III), Hg(II), and Zr(IV) are indicated. Pu(III) and the pentavalent and hexavalent actinides are also reported to interfere. However, the data presented on the effect of interfering elements were limited to the Np determination; uranium(VI) did not interfere. The method can be used for samples containing from 0.05 to 50 mg of these quadrivalent actinides in $HClO_4$, HCl, or HNO_3. The average precision and accuracy was 1.0% for quantities of 239 to 717 μg of Pu.

Survey of Production Facilities

No routine data were available from the users' survey.

Survey of Exchange Programs

This method was not evaluated by the exchange programs.

4.9.4 Controlled-Potential Coulometry

Description of Method

Controlled-potential coulometry (CPC) may be regarded as a special kind of redox titration in which electric current is used as the titrant. In comparison with most redox titrations, coulometry achieves high precision with 5- to 15-mg quantities of Pu in the presence of large amounts of U, Al, and nitrate. As a result, the technique has been widely applied to the determination of Pu in irradiated nuclear fuel solutions as well as in unirradiated materials. Coulometry readily lends itself to remote operations.

In analysis by CPC, the species to be determined is quantitatively electrolyzed at an electrode whose potential is maintained at such a value that unwanted electrode reactions are precluded. The potential of the working electrode is controlled by means of a potentiostat.

In a normal electrolysis, the current decreases exponentially as the reaction proceeds, until a background current is attained. The electrolysis is then terminated. From the quantity of electricity required by the reaction (measured by means of a current/time integrator), the amount of the substance being determined can be calculated, using a form of Faraday's Law:

$$w = \frac{M}{nF}\int_0^t i\,dt \qquad (4\text{-}39)$$

$$= \frac{MQ}{nF}$$

where

w = weight of Pu electrolyzed, g
M = gram-atomic weight of Pu (adjusted for isotopic composition)
i = electrolysis current, amperes
t = time of electrolysis, s
n = number of electrons involved in the overall reaction
F = Faraday constant, 96,487 coulombs/mole (based on the relative atomic mass of ^{12}C as 12)
Q = quantity of electricity, coulombs

The calculation assumes that only one electrochemical reaction (in this case, reduction) occurs with the element being measured. Therefore, conditions must be precisely controlled so that all of the current passing through the coulometric cell produces the desired electrochemical reaction; i.e., the current efficiency is 100%. Impurities, including dissolved oxygen and carbonaceous material, that can interfere by being electrolytically oxidized or reduced under the conditions of the coulometric determination, must be removed. Detailed discussions of the theory and applications of controlled-potential coulometry are available (Refs. 186 to 189).

The amount of Pu present can also be calculated from calibrations of the instrument obtained by the analysis of standard solutions (chemical calibration). Many workers prefer chemical calibration to reliance on the Faraday Law (electrical calibration).

The majority of coulometric methods for Pu are based on the electrode reaction:

$$\mathrm{Pu(IV)} + e \rightleftharpoons \mathrm{Pu(III)} \qquad (4\text{–}40)$$

The Pu(III)-Pu(IV) couple behaves reversibly under suitable electrolytic conditions, and current efficiencies of nearly 100% are attainable. Consequently, Pu can be adjusted to either the trivalent or quadrivalent state by electrolytic pretitration and then determined by coulometric conversion to the other oxidation state. The method was originally developed by Scott and Peekema (Ref. 304). The comprehensive review by Shults (Ref. 305) is still definitive.

Coulometric titrations can be performed with molar solutions of perchloric acid, hydrochloric acid, sulfuric acid, or nitric acid as supporting electrolyte. Shults (Ref. 305) preferred 1*M* $HClO_4$ medium because the Pt electrode requires less attention and reagent blanks obtained in that medium are insignificant when 1 mg or more of Pu is titrated. The use of 0.5*M* H_2SO_4 is preferred for samples that contain appreciable quantities of Pu(VI) because Pu(VI) can be quantitatively reduced to Pu(III) in that medium. Also, if the titration follows a depolymerization or an ion-exchange separation, or if the sample was dissolved in a mixture of nitric and hydrofluoric acids, the solution is fumed with sulfuric acid to remove fluoride and/or organic impurities, is diluted, and is then titrated in the sulfuric acid solution. Plutonium (VI) is only partially reduced to Pu(III) in solutions of the other mineral acids. However, Fe interferes quantitatively with the Pu determination in H_2SO_4 because Fe and Pu are reduced and oxidized at essentially the same potentials in sulfate medium. It is thus necessary to determine Fe spectrophotometrically in a separate aliquot of the solution and to apply a correction to the Pu results.

In other mineral acid media, the potentials of the Pu(IV)-Pu(III) and Fe(III)-Fe(II) couples are 0.20 to 0.25 V apart. It is possible to minimize the effect of Fe in these media by restricting the range of working potentials somewhat. For a reversible one-electron reaction, such as the reduction or oxidation of Pu(IV) or Pu(III), and for a degree of completion of 99.9%, a potential span of $E^\circ \pm 0.18$ V is generally selected (where E° is the formal potential). If the potentials are selected so that the reactions do not proceed to completion, but the extent of reaction is known, a correction must be applied.

In 0.5*M* H_2SO_4, the formal potential of the Pu(IV)-Pu(III) couple is 0.49 V versus an SCE. To carry out the coulometric measurement, Pu(IV) and Pu(VI), if present, are reduced to Pu(III) at +0.31 V versus SCE. Plutonium (III) is then oxidized to Pu(IV) at a potential of +0.67 V versus SCE. Similarly, in 1*M* $HClO_4$ where $E^\circ = 0.715$ V, control potentials of +0.535 V versus SCE (+0.555 V in the presence of Fe) and +0.895 V versus SCE are used for the reduction and oxidation steps (Ref. 305). Table 4.36 lists the formal redox potentials of the Pu(IV)-Pu(III) and Fe(III)-Fe(II) couples in various media.

Table 4.36 Formal redox potentials of Pu(III)−Pu(IV) and Fe(II)−Fe(III) couples in various media[a]

Medium	Concentration (*M*)	E° (V vs SCE)	
		Pu	Fe
$HClO_4$	1.0	0.715	0.465
	2.5	0.72	0.47
	5.0	0.73	0.46
HCl	0.1	0.76	0.51
	0.25	0.75	0.49
	1.0	0.72	0.45
	3.0	0.68	0.39
	5.0	0.64	0.31
HNO_3	0.5	0.69	0.48
	1.0	0.69	—
	1.5	0.65	—
	2.0	0.64	—
H_2SO_4	0.25	0.50	—
	0.5	0.49	0.45
	1.0	0.48	0.45
	2.5	0.46	—
	5.0	0.43	—

[a] From Ref. 305.

Scope of Applications

Controlled-potential coulometry has been applied to a wide variety of Pu materials, ranging from relatively pure Pu solutions to high-fired oxides, carbides, and nitrides and irradiated nuclear fuels. Many procedures have been devised to adapt the technique to new and different types of materials. A listing of some of these is given in Table 4.37. Platinum or gold mesh electrodes or mercury pools have been used as working electrodes. In general, samples containing 5 to 15 mg of Pu per determination are used.

Controlled-potential coulometry is especially well suited to the analysis of irradiated material, since only a few milligrams are required for a determination. Furthermore, the method lends itself to remote operations, since only the coulometric cell needs to be inside the glovebox or hot cell. The electronics can be outside and some distance away.

Summary of Performance

Table 4.38 lists the performance of the method as applied to different Pu-containing materials. Although specific method details were generally not available some are listed later in this section when the literature, user, and exchange program methods are discussed.

Equipment

In CPC, the substance determined is electrolyzed at a working electrode, the potential of which is controlled or maintained constant during the electrolysis by means of a potentiostat, and the current is integrated by means of an electronic integrator or coulometer. A typical experimental arrangement for this technique is shown in Figure 4.12. The counter electrode is placed in a separate cell compartment connected to the sample solution through a semipermeable separator to prevent reversal of the desired working-electrode reaction. The solution is stirred vigorously to effect a rapid electrolysis. The time for a normal electrolysis is 15 min.

Instrumentation

Potentiostats, integrators, and digital voltmeters are commercially available from many sources. Some desirable specifications for these instruments follow.

Potentiostat and Integrator

The potentiostat should have an output capability of >200 mA and >10 V, an input current of <50 nA, and a full-scale current-meter range of 100 μA or less. The integrator must have a full-sçale range of at least 20 coulombs. In terms of a readout of mass of Pu, the output drift rate should be adjustable to <0.2 μg/min and should remain stable within ±0.5 μg per 15 min per month. The electrical calibration of the integrator should remain within ±0.1% per year.

Table 4.37 Some methods for the determination of plutonium by controlled-potential coulometry[a]

Type of Materials	Working Electrode	Supporting Electrolyte	Control Potentials or E° (V vs SCE)	Interferences, Comments	Ref.
Reactor fuel solutions	Pt	1*M* $HClO_4$, 1*M* HNO_3, 1*M* HCl, 1*M* H_2SO_4	E° = +0.72, +0.69, +0.72, +0.48	Interferences: Au(III), Pd(II), F^-, Hg(II) (ex. in HCl), Fe (worse in H_2SO_4), Zr, V.	304, 305
Reactor fuel solutions	Hg	1.0*M* Potassium Citrate, 1*M* $Al_2(SO_4)_3$; pH:4.5	E° = 0.19	Higher tolerance to Hg(II), Ag, Au; lower tolerance to U(VI), Cu(II), Fe, Mo(VI), O_2, Ru, Pb(II), and Sn(IV) than mineral acid media.	304
Reactor fuel solutions	Pt or Au	0.5*M* H_2SO_4	+0.33, +0.69	High-speed electrolysis cell used.	306
Pu-U oxides, Pu-Th oxides	Pt	1.0*M* H_2SO_4	+0.30, +0.70	Dissolution via fusion in NH_4HSO_4; V, Ta, Nb interference studied.	62
PuO_2	Pt	1.0*M* H_2SO_4	+0.30, +0.70	Dissolution via fusion in Na_2O_2/NaOH.	61
Pu-U oxides	Hg	0.5*M* H_2SO_4, 0.2*M* NH_2SO_3H	+0.055	Dissolution in $HNO_3/H_2SO_4/(NH_4)_2SO_4$. Determination of U at −0.395 V.	203
Reactor fuel solutions	Au	0.5*M* HNO_3, 0.01*M* NH_2SO_3H	+0.86, +0.50	Prior anion-exchange column separation of Pu.	307, 10[b]
Pu-U solutions	Pt	2*M* HCL, 1*M* H_2SO_4, 0.6 m*M* Bi(III), 0.1*M* NH_2SO_3H	+0.20, +0.80 +0.20, −0.20	Consecutive determination of Pu and U. Bi inhibits H_2 evolution. Reaction at Pt electrode surface unstable.	190
Pu-U oxides, carbides, and nitrides	Pt	0.5*M* H_2SO_4	+0.31, +0.67	Various dissolution procedures. Determination of U at Hg electrode. Studied effects of W, ^{238}Pu, ^{241}Pu, ^{241}Am. No separations required to 6 at. % burnup.	53, 54

Note—See footnote at end of table.

Table 4.37 Some methods for the determination of plutonium by controlled-potential coulometry[a] (Cont'd)

Type of Materials	Working Electrode	Supporting Electrolyte	Control Potentials or E° (V vs SCE)	Interferences, Comments	Ref.
$(Pu, U)O_2$ fuel	Pt	1.0M HClO	+0.535, +0.895	Dissolution in HNO_3/HF.	204
$^{238}PuO_2$ fuels	Pt	1M HCl	+0.54, +0.90	Procedure avoids radiolysis effects. Reduction of Pu with Pb reductor.	25
Pu-U mixtures	Au	0.2M H_2SO_4, 1.0M HNO_3, 0.2M NH_2SO_3H	+0.29, +0.69, +0.29	U also determined. Prereduction with Ti(III); reaction of U(IV) with Pu(IV).	308
Pu-U solutions	Pt	4.5M HCl, 0.5mM Bi(III)	+0.26, +0.15, −0.2	Consecutive determination of Pu and U; plutonium oxidized to Pu(VI) with perchloric acid; Pu(VI)-Pu(III) couple used.	209
Pu solution	Pt	5.5M HCl, 0.015M sulfamic acid NaH_2PO_4	0.25, 0.57, 0.68	Phosphate added to reduce Pu(III)-Pu(IV) potential. High tolerance for diverse ions, especially iron.	309

[a] Table adapted from Ref. 189.

[b] Pages 385-388.

Table 4.38 Summary of performance: determination of plutonium by controlled-potential coulometry

Application	Performance (% RSD)		
	Random Error	Systematic Error	Source[a]
PuO_2 powder	0.05	—	L
	0.019[b]	0.045	U
	0.26	—	E
Pu metal	0.17	0.045	U
	0.024, 0.025	—	E
$(Pu,U)O_2$ powder	0.082, 0.088	—	E
$(Pu,U)O_2$ pellets	0.15	—	L
	0.19	—	E
(Pu,U)C pellets, 19% Pu	0.29[b]	0.045	U
UO_2 + PuO_2 + C, 16% Pu	2.8[b]	0.045	U
$Pu(NO_3)_4$	0.12, 0.21	—	E
Dissolver solutions	1.1	—	L

[a] E = survey of exchange programs;
L = literature survey;
U = users' survey of production facilities.

[b] Includes sampling error.

Digital Voltmeter

The readout digital voltmeter should be a full four-digit instrument (i.e., capable of indicating 9.999) with a 100% over-range being desirable. The accuracy specification should equal or exceed the following: ±(0.02% of reading +0.01% of full scale) for 6 months at an operating temperature of 25°C ± 5°C.

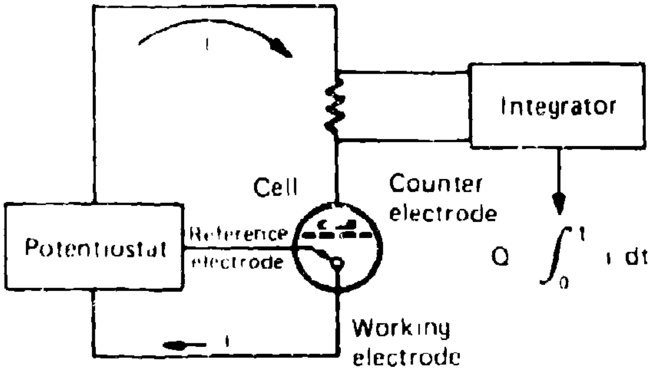

Figure 4.12 Block diagram of apparatus for controlled-potential coulometry (taken from Ref. 189).

Electrolysis Cell

The accuracy and precision of CPC are strongly dependent on the design of the electrolysis cell. Some of the design criteria are the speed of electrolysis, speed of solution deoxygenation, uniformity of dc potential distribution at the working electrode, convenience of use, and reliability.

A variety of cell designs are described in the literature (Refs. 53, 304, 306, and 310). A cell that has been widely used with excellent results is shown in Figure 4.13. Details regarding the cell construction, assembly, and operation may be found in Reference 43.

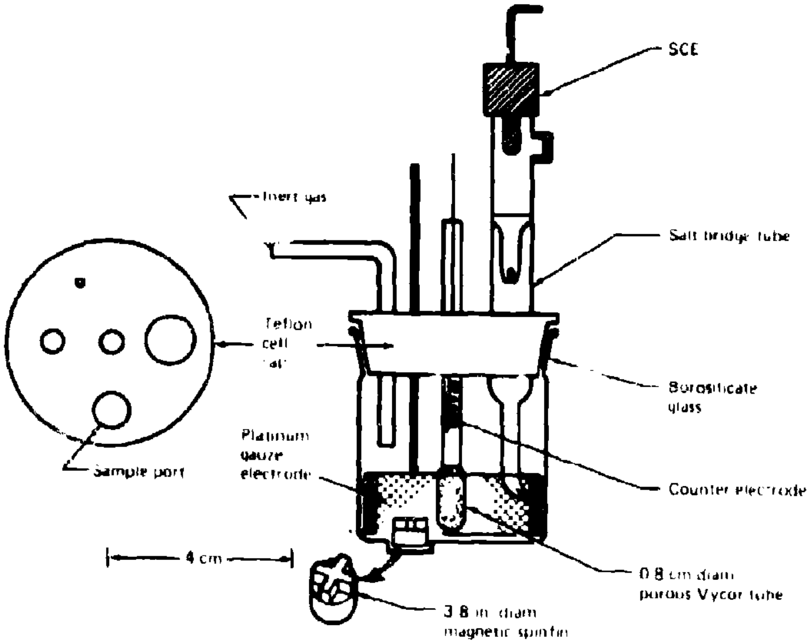

Figure 4.13 Controlled-potential coulometry electrolysis cell.

Major Sources of Error

The errors most commonly encountered result from the following:

(1) Uncertainty in the value of the standard used for instrument calibration
(2) Accuracy uncertainty of the analytical balance
(3) Inadequate removal of oxygen from the cell before and during the electrochemical steps

(4) A malfunctioning reference electrode causing a shift in the actual control potential
(5) Inadequate operator techniques

Interferences in 0.5*M* sulfuric acid medium are caused by ions that are electroactive at the reduction-oxidation potentials used or by species that prevent the complete reduction or oxidation of the Pu.

Polymerized Pu is not electroactive, but it may be determined after depolymerization by treating the sample with HF and fuming with H_2SO_4 (Ref. 305).

Organic matter such as degradation products from ion-exchange resins cause interference by fouling the Pt working electrode. This is manifested by low initial electrolysis currents, extended electrolysis times, and low results in the determinations. This interference can usually be removed by fuming the sample with H_2SO_4, H_2SO_4/HNO_3, or $HClO_4$.

Zirconium, Ta, and Nb, even though not electroactive, may interfere in a manner similar to that of organic matter (Ref. 62, 305). The tolerance to these elements has not been carefully studied, but is known to depend on solution aging and pretreatment effects. Plutonium-to-element mole ratios less than 1000:1 should cause concern. The formal potential of the Fe(III)-Fe(II) couple in 0.5*M* H_2SO_4 is +0.45 V versus SCE, thus Fe is almost quantitatively reduced and oxidized at the potential used for the Pu determination. For less than 0.1% positive bias, the Pu/Fe weight ratio must be greater than 4260:1, or the quantity of Fe as an impurity with respect to the Pu must be less than 235 ppm.

Anions that complex Pu(IV) more strongly than does sulfate also interfere because such complexation shifts the formal potential of the Pu(IV)-Pu(III) couple, thus preventing complete reduction of the Pu(IV) at the recommended control potential. Examples of such interferences are fluoride and phosphate; in addition, amounts of sulfate causing the cell solution to be greater than ≈1.0*M* SO_4^{2-} will also cause a negative bias. Fluoride can be removed from the sample by fuming with H_2SO_4, or it can be masked with Al(III). Phosphate can be removed by means of an anion-exchange procedure. Nitrite and nitrogen oxides interfere but are removed by reaction with sulfamic acid.

Oxygen interferes seriously with the electrolysis. It is mandatory that the sample solution be purged of oxygen before electrolysis and that an inert gas blanket be maintained within the cell throughout the electrolysis.

A great amount of work has been done to devise a means of removing the interference of Fe. The method of Jackson et al. (Ref. 309) is of special interest, because it has extremely high tolerance for Fe and some 50 other metal ions. In this procedure, Pu is reduced to Pu(III) at +0.25V versus SCE in a 5.5*M* hydrochloric acid/0.015*M* sulfamic acid electrolyte. Diverse ions are oxidized at +0.57 V, phosphate is added to reduce the Pu(III)-Pu(IV) potential, and Pu(III) is oxidized to Pu(IV) at 0.68 V.

Many anions are without effect and most interfering ones are removed by a preliminary fuming with perchloric acid. An automated coulometer has been used. The precision of the method is better than 0.1% at the 5-mg Pu level.

Measurement Control Requirements

Chemical calibration of the instrument is preferred to electrical calibration, because the latter can introduce a bias in the determination of Pu. The standard solution used for calibration should closely resemble the samples to be analyzed.

Instructions for chemical calibration and determining the background current are found in References 43 and 203. The chemical calibration factor and the background correction should be verified daily or at the beginning of each shift.

Data Analysis Requirements

Calculate the Pu assay of the sample as follows:

$$\mathrm{Pu} = \frac{(S - B)F_c A}{X} \tag{4-41}$$

where

Pu = grams of Pu per gram of sample
S = integrator readout voltage for electrolysis of sample aliquot
B = integrator readout voltage for background electrolysis
F_c = chemical calibration factor, equivalents of Pu per volt of readout
A = equivalent weight of Pu (adjusted for isotopic composition)
X = mass of sample aliquot, g

The chemical calibration factor is calculated as follows:

$$F_c = \frac{E_{\mathrm{Pu}}}{D - B} \tag{4-42}$$

where

E_{Pu} = equivalents of Pu in aliquot of standard solution
D = integrator readout voltage for electrolysis of standard

If electrical calibration has been performed and a Pu sample is then analyzed, the theoretical recovery is 99.82% for a potential span of

±180 mV. The quantity of Pu present is calculated according to the following equation:

$$W = 1.0018\,\frac{MQ}{nF} \tag{4-43}$$

where

W = grams of Pu present
M = gram-atomic weight of Pu (adjusted for isotopic composition)
Q = quantity of electricity, coulombs
n = number of electrons involved in the electrode reaction (equals 1)
F = Faraday constant, 96,487 coulombs pe. gram equivalent

Survey of Selected Literature

For controlled-potential coulometry in 0.5*M* sulfuric acid medium, a precision of 0.1% RSD or better can be readily attained.

In the analysis of high-fired PuO_2, dissolved by fusion with anhydrous potassium sulfate and sodium peroxide, and taking up the melt in 1*N* NHO_3 + 1*N* H_2SO_4, a precision or 0.05% RSD was claimed (Ref. 64).

In interlaboratory studies of the analysis of mixed (U,Pu) oxide pellets, a single laboratory obtained 0.07% RSD for the Pu determination. The pooled RSD value obtained by six laboratories was 0.15% for Pu (Ref. 53 and 208).

In the analysis of highly radioactive dissolver solutions (Ref. 307), Pu was separated by anion-exchange from Fe and fission products. The Pu recovery was 101%, and the precision was 1.1% RSD.

Survey of Production Facilities

Routine performance data were obtained from one facility. In this method approximately 2 mg of Pu in 0.5*M* H_2SO_4 is electrolyzed at a Pt cathode. The solution is prereduced at +0.310 V versus SCE, and the Pu(III) oxidized to Pu(IV) at +0.670 V. An electrical calibration is performed approximately 2 times each year. Results, however, are based on a chemical calibration factor determined for each group of samples run, or, at a minimum, twice a week. The method is applied to the following materials with random errors as listed:

Material	Random Error (% RSD)
Pu metal	0.17
PuO_2 powder	0.19 (includes sampling error)
(Pu,U)C pellets (19% Pu)	0.29 (includes sampling error)
$UO_2 + PuO_2$ + C (16% Pu)	2.8 (includes sampling error)

A systematic error of 0.045% RSD was determined for the method by statistically combining the random error of the mean of the replicate standard determinations and the uncertainty of the standards certified value.

Survey of Exchange Programs

The SALE (Ref. 154) program evaluates controlled-potential coulometry as a method for determining Pu in PuO_2, $(Pu,U)O_2$, and $Pu(NO_3)_4$ materials. Specific method details, however, are not available for the different laboratory participants. The laboratory random errors reported for the method as applied to the selected materials are as follows:

Material	Random Error (% RSD)
PuO_2 powder	0.26
$(Pu,U)O_2$ powder	0.082, 0.088
$(Pu,U)O_2$ pellets	0.19
$Pu(NO_3)_4$	0.12, 0.21

Two laboratories participating in the plutonium metal sample exchange program employ CPC to determine Pu in Pu metal (R. L. Carpenter, Rocky Flats Plant, unpublished information, Sept. 1979-June 1980). In the method of one laboratory, the sample is electrolyzed at a Pt working electrode in a 0.5*M* H_2SO_4 supporting electrolyte. The sample is prereduced at +0.31 V versus SCE and the Pu(III) oxidized to Pu(IV) at +0.67 V. A random error of 0.025% RSD was obtained for the method. The method of the second laboratory calls for a gold working electrode and a 1*M* HNO_3 supporting electrolyte. A random error of 0.024% RSD was obtained for the method.

4.9.5 Spectrophotometry

Description of Method

The spectrophotometric determination of Pu is based on the absorption of light of a specific wavelength by Pu compounds or complexes in solution. The fraction of incident light that is absorbed is proportional to the concentration of the absorbing species. The relationship is written

$$\log \frac{I_0}{I} = abc = A \qquad (4\text{–}44)$$

where

I_0 = intensity of the incident radiation
I = intensity of the transmitted radiation
a = absorptivity

b = path length
c = concentration of the substance
A = the absorbance (sometimes referred to as optical density or extinction)

The molar absorptivity, ε (sometimes referred to as molar extinction coefficient), is the product of the absorptivity a and the molecular weight of the substance.

Beer's Law states that the absorptivity of a substance is a constant with respect to changes in concentration. The measured absorbance will thus vary linearly with concentration. However, deviations from this relationship may occur at high concentrations or is a result of competing reactions.

Aqueous acid solutions of Pu may contain the element in the trivalent, quadrivalent, or hexavalent forms, or, less commonly, in the quinquivalent form. Each of the individual oxidation states of Pu has a characteristic absorption spectrum, consisting mostly of narrow bands. The complete spectra of all the Pu ions were first recorded by Cohen (Ref. 311). Some of these characteristic absorption bands have been widely used for the determination of total Pu in solution and for the identification and determination of the individual oxidation states. Table 4.39 is a compilation of the prominent absorption bands of each oxidation state. In Table 4.40, one absorption band, shown in bold type, has been selected as most suitable for the identification or determination of each oxidation state. The absorptivities of other oxidation states at those wavelengths are also given. It is thus necessary, when total Pu is to be determined, to be sure that all the Pu is in the one desired oxidation state. Alternatively, measurements at more than one wavelength must be made and a correction applied for the absorbance of the other oxidation states present.

The molar absorptivities given in Tables 4.39 and 4.40 apply only for the solvent and at the temperature given. The wavelengths and molar absorptivities of the absorption bands depend on the solvent and its concentration, the temperature, and complex formation. For instance, studies of the chloride complex ions of Pu(VI) showed a decrease in the molar absorptivity of the 830-nm band with increasing chloride concentration. Comparison of spectra of Pu(VI) in $2M$ $HClO_4$ and $2M$ HCl showed a shift of the band maxima to higher wavelengths (Ref. 314). A detailed study of acetate complexes of Pu(VI) showed a decrease in molar absorptivity and a shift of the absorption maximum to higher wavelengths with increasing pH (Ref. 315). Ryan (Ref. 316) studied the absorption spectra of Pu(IV) in 3 to $15.5M$ HNO_3 solutions and found shifts of the absorption maxima to lower wavelengths with higher acid concentration.

If Pu is to be determined by spectrophotometry of an absorption band of an individual state, the temperature and acid concentration must be reproducibly controlled. This applies especially if the Pu concentration is to be calculated from the molar absorptivity. However, control of solvent and temperature is necessary also if standards are prepared and a calibration curve is constructed.

Table 4.39 Prominent absorption bands of plutonium oxidation states in dilute acid solution[a]

Oxidation State	Wavelength (nm)	Molar Absorptivity ($L \cdot mol^{-1} \cdot cm^{-1}$)	Solvent
Pu(III)	900	19.3	0.1*M* $HClO_4$, 25°C
	665	14.6	0.1*M* $HClO_4$, 25°C
	603	35.4	0.1*M* $HClO_4$, 25°C
	560	36.1	0.1*M* $HClO_4$, 25°C
Pu(IV)	815	19.6	0.5*M* HCl, 25°C
	730	14.6	0.5*M* HCl, 25°C
	655	34.4	0.5*M* HCl, 25°C
	470	49.6	0.5*M* HCl, 25°C
Pu(V)	1130	22.0	0.2*M* $HClO_4$, 10°C
	995	4.1	0.2*M* $HClO_4$, 10°C
	850	8.0	0.2*M* $HClO_4$, 10°C
	775	9.0	0.2*M* $HClO_4$, 10°C
	569	17.1	0.5*M* HCl
Pu(VI)	983	24.2	1*M* $HClO_4$
	953	24.4	1*M* $HClO_4$
	830	555.0	1*M* $HClO_4$
	522	12.0	1*M* $HClO_4$
	504	13.5	1*M* $HClO_4$
	458	12.8	1*M* $HClO_4$

[a] Adapted from Ref. 312.

Table 4.40 Molar absorptivities of the most suitable absorption bands for identification and determination of the individual oxidation states of plutonium.[a, b]

Wavelength (nm)	Molar Absorptivities ($L \cdot mol^{-1} \cdot cm^{-1}$)[c]			
	Pu(III)	Pu(IV)	Pu(V)	Pu(VI)
470	3	**49.6**	2	11
603	**35.4**	2	2	1
830	5	16	5	**555**
1130	16	13	**22**	0

[a] Adapted from Ref. 313.
[b] All solutions, except Pu(V), in 1*M* $HClO_4$ at 25° C. Pu(V): 0.2*M* $HClO_4$ at 10°C.
[c] Most suitable band for each oxidation state in bold.

Determinations of Pu by use of a characteristic absorption band of an oxidation state will be referred to as "direct determination." Because the molar absorptivities of these absorption bands are generally low, direct determinations are primarily for higher concentrations of Pu or samples where Pu is a major constituent.

There are a number of chromogens that react with Pu to form colored complexes. These complexes generally have high molar absorptivities and are suitable for the determination of low concentrations of Pu. Use of a chromogenic method generally requires that all the Pu be in the same appropriate oxidation state. Since Th, U, and many other cations may form colored complexes with the chromogens that react with Pu, a separation is normally required. Nuclear methods, such as alpha or gamma-ray spectroscopy, may be preferable for the determination of Pu in solution at low concentrations.

Spectrophotometric methods for the determination of Pu have been reviewed by several authors (Refs. 76, 317, and 318).

Scope of Applications

Spectrophotometric procedures may be applied to the determination of Pu in a variety of materials, such as dissolver solutions, waste solutions, and product streams. Spectrophotometric methods have also been applied to the determination of the Pu content of Pu metal and Pu oxide, after dissolution of the solid.

Direct spectrophotometric methods are usually applied to the determination of high concentrations of Pu in solution, or to samples in which Pu is a major constitutent. The precision of direct methods is generally poorer than 0.5% RSD, and often 1% to 2%. Differential spectrophotometric methods (Ref. 214) were developed to improve the precision, so that the relative standard deviation of the measurements would decrease to a level of 0.1% to 0.5% or less. The increased precision is achieved by an appropriate expansion of the scale used for the measurement of light intensities. Scale expansion can be made by placing cuvettes containing solutions of suitable concentrations in the cell compartment of the instrument and adjusting the transmission (or absorbance) scale with them. In the "transmittance ratio method" the unknown solution is compared with a known solution of slightly lower concentration. In the "ultimate precision method" two reference solutions are needed; one is more concentrated than the unknown solution, the other is less concentrated. Reference 214 is an excellent review of differential spectrophotometry. Differential spectrophotometry can yield an accuracy and precision comparable to those obtained with titrimetric methods (Refs. 319 and 320). The technique may be valuable for the determination of Pu in dissolver solutions and product streams.

Chromogenic methods are used for the determination of microgram quantities of Pu. Relative standard deviations generally fall in the 0.5% to 2% range. Solutions containing fission products or other interfering ions require a Pu separation prior to spectrophotometry. The tetrapropylammonium nitrate method (Ref. 122) can be used for sequential determination of U and Pu. The method has been automated (Ref. 217).

Summary of Performance

Some of the spectrophotometric methods that have been used for the determination of Pu are summarized in Table 4.41. The concentration range or amount of Pu required per sample, the precision of the method, and interferences are listed. Additional details for these and other similar methods are presented in "Survey of Selected Literature" later in this section.

Equipment

Direct or differential methods require a high-precision recording spectrophotometer with double monochrometer, a band-bass of 1 nm or less, variable slit width, and temperature-controlled sample chamber (control within 0.2°C is required for differential methods). A dual-beam instrument is preferred for differential methods. Digital readout is desirable. Wavelength accuracy should be within 0.3 nm, and wavelength reproducibility within 0.1 nm. Photometric accuracy and reproducibility should be 0.15% between 1 and 2 absorbancy units. The wavelength range required will depend on the analyses to be performed with the instrument. If analyses are done with the 831 nm band of Pu(VI), the range of the spectrophotometer should extend to 950 or 1000 nm. Instruments with these specifications cost approximately $10,000.

For many chromogenic methods (but not the tetrapropylammonium method), a nonrecording spectrophotometer with 10 nm (or less) bandpass is adequate. Digital readout, rather than meter readout, is desirable. A single-beam instrument that covers the 325- to 925-nm wavelength range will cost about $3000.

Major Sources of Error

Sources of error in spectrophotometric methods include volumetric errors, such as in pipetting, dilution, or making solutions up to a specified volume; incomplete separation or improper oxidation state of Pu; presence of other oxidation states besides the one desired; failure to set the spectrophotometer to the absorption band maximum; and differences in composition between standards and samples. Temperature control to 0.2°C is required for direct and differential spectrophotometry (Ref. 214). Interferences encountered in specific methods are listed in Table 4.41 and detailed in the "Survey of Selected Literature."

Table 4.41 Some spectrophotometric methods for the determination of plutonium

Ion or Chromogen	Application	Relative Standard Deviation (%)	Interferences, Comments	Ref.
Pu(III), 565 nm	Pu solutions, 8 to 14 mg/mL	0.05	Al, Fe(III), Zr, Mo; differential spectrometry.	319
Pu(VI), 830 nm	Pu solutions, 0.2 to 140 mg/L	2.9 to 2.0 (7 to 140 mg/L)	Mn, chloride, phosphate, sulfate.	321
Pu(VI), 830 nm	Reprocessing solutions, a few milligrams per liter to several grams per liter	3 to 0.2 (50 to 250 mg/L)	Mn, chloride, phosphate, sulfate; neodymium internal standard.	322
Tetrapropyl-ammonium	(Pu,U) solutions, 0.5 to 14 mg/0.5 ml	2.0 to 0.2 (2 to 20 mg/mL)	Cr, Th, sulfate, fluoride.	217
Arsenazo-III	Purex solutions, 1 to 15 μg	1.9 to 0.58 (2 to 10 μg)	No interferences after recommended separation.	323
Xylenol orange	Reprocessing solutions, 1 to 6.5 μg/mL	0.3 to 0.1 (2 to 5 μg/mL)	Th, Zr; tolerates moderate amounts of U(VI), phosphate, fluoride.	324

Measurement Control Requirements

An aliquot of a standard solution, prepared from a primary standard such as NBS 949, should be analyzed at least once each shift. A control chart based on the average value should be established. Changes in the measured value at the 0.05 significance level require investigation of the reasons for the change before samples are analyzed. A second aliquot should be analyzed to rule out operator error as the cause of the change. If the second analysis confirms the results of the first, a complete recalibration should be done. Any changes in analysis conditions also make recalibration mandatory.

The precision of the method should be checked routinely by performing replicate analyses (at least 5 determinations) of known solutions. It is recommended that standard solutions having Pu concentrations at the low end, middle, and high end of the range of the method be analyzed.

Data Analysis Requirements

In one method of calculating the Pu content of a sample, a series of standard solutions of known Pu concentration are used to obtain an average calibration factor (concentration of Pu per absorbance unit). The measured absorbance of the sample (corrected for blank and background), the calibration factor, and the volume of the sample are used to calculate the quantity of Pu in the sample. Alternatively, a calibration equation can be obtained by a least-squares fit of the calibration data. The Pu concentration in the samples can be calculated with the derived equation. Plutonium concentrations can also be calculated with the correct molar absorptivity for the system under examination.

Survey of Selected Literature

In the following discussions of individual procedures, the direct, differential, and tetrapropylammonium methods are emphasized. Methods involving such chromogens as xylenol orange, thoronol, and arsenazo are not widely used.

Direct and Differential Spectrophotometry

The direct and differential methods employ characteristic absorption bands of Pu(III) or Pu(VI). For the determination of Pu as Pu(III), the absorbance of the solution is measured at either 560 or 603 nm. Determinations of Pu(VI) involve measurement of the strong absorption band at 830 nm.

The direct measurement of the 603-nm band of Pu(III) has been used for the determination of Pu concentrations of 2- to 4-mg/L in cells with 1-cm light paths. The precision of the determination was "within 1%." The method was applied to the analysis of dissolver solutions. An ion-exchange separation preceded spectrophotometry. Plutonium in the tetravalent state was absorbed on an anion exchange resin from 10*M* HNO_3, and other metals were washed from the column with this eluant. Plutonium was reduced to Pu(III) and eluted with 10% hydroxylamine hydrochloride, the eluate centrifuged, and the absorbance of Pu(III) was measured at 603 nm (Ref. 317).

Precise determinations of Pu as Pu(III) have been made by the transmission ratio method of differential spectrophotometry. In all cases, the absorbance of the solution was measured at 560 or 565 nm. In the procedure described by Phillips (Ref. 319), Pu metal or Pu-Th alloys were dissolved in hydrochloric acid and Pu was reduced to the trivalent state by an excess of hydroxylamine hydrochloride. The absorbance was measured relative to an accurately known standard containing 8 mg Pu/mL. Measurements could be made within the range of 8 to 14 mg Pu/mL with a relative standard deviation of 0.05% for pure Pu solutions. Thorium, U, Ca, and Ce(III) do not interfere at molar ratios as high as 8:1. Trivalent iron interferes, even at ratios of Fe to Pu as low as 0.1. The interference from Fe(III) can be overcome to some extent by the addition of stannous chloride. Aluminum causes a slight decrease in absorbance at ratios of 1.5 and greater, while Zr increases the absorbance. When Pu solutions containing large excesses of noninterfering impurities or alloying elements were analyzed, the bias was less than 0.3%, and the relative standard deviation was less than 0.4%. Measurements were made at 25.0°C ±0.2°C.

A similar procedure (Ref. 325) was applied to the determination of the Pu content of plutonium dioxide that had been fired at 850°C or 1550°C. A 100-mg sample of plutonium dioxide was sintered at 400°C with sodium peroxide and then with sodium hydroxide. The cold sinter was extracted with water and then transferred to a hydrochloric acid solution containing hydroxylamine hydrochloride. The solution was heated to decompose the peroxide and reduce Pu to Pu(III). The Pu determinations were made by differential spectrophotometry at 565 nm against standards prepared from Pu metal. Analysis of 10 replicate samples of plutonium dioxide ignited at 850°C gave a mean recovery of 99.81% and a relative standard deviation of 0.3%. For eight analyses of oxide ignited at 1550°C, the mean recovery was 99.85% and the relative standard deviation was 0.2%.

In the analysis of samples by differential spectrophotometry, the solution should be diluted to give an absorbance of less than 1.0, and a preliminary assessment of the Pu concentration made by direct spectrophotometry. When the approximate concentration of Pu in the sample is known, a standard having a slightly lower concentration of Pu is selected. The difference in absorbance between the unknown and the reference standard is measured, and the Pu concentration is calculated by using the calibration factor.

Winters (Ref. 320) studied the differential spectrophotometric determination of Pu(III). Instead of using reference solutions, he measured the absorbance of unknown solutions against colored glass filters of known absorbances. The relative standard deviation of the calibration data was about 0.03% in the 11- to 15-g Pu/L range. He estimated that the relative standard deviation for the analysis of an unknown Pu solution would be approximately 0.05%.

The strong absorption band of Pu(VI) near 830 nm has been used for the determination of Pu in the presence of other elements. Values reported for the molar absorptivity of the band in various media are 550, 554.7, and 555 ± 5 (Refs. 311, 314, and 315). A slit width of 0.15 nm was used in the determination of those values. Since the band is sharp (the half width is 2.7 nm), the observed absorbance is dependent on the resolution of the spectrophotometer, and hence on the slit width (Ref. 315). A high-resolution recording spectrophotometer, preferably double-beam, with variable slit width that can be accurately and reproducibly set, and with scale expansion facilities, is required (Ref. 321). It is also desirable to be able to control the temperature of the sample and reference solution compartment. The photomultiplier used must have a high signal-to-noise ratio in the near infrared (Ref. 322).

Two procedures based on the strong absorption band of Pu(VI) are of interest. The first procedure (Ref. 321) is applicable to solutions containing Pu in the range of 0.2 to 140 mg/L. In the recommended procedure, an aliquot of sample solution containing from 0.01 to 7 mg of Pu is made 4 *N* in nitric acid. The fixed volume should not exceed 40 mL. Silver (II) oxide is added to oxidize Pu to the hexavalent state. The excess silver (II) oxide is destroyed by heating the solution to near boiling. The solution is cooled, transferred to a 50-mL volumetric flask, and made up to volume with 4*N* nitric acid. The absorption spectrum of the solution is recorded from 750 to 900 nm in a 10-cm cell against 4*N* nitric acid as a blank. The scope of the procedure can be increased to higher concentrations by using cells with shorter optical paths.

In the above procedure, several common anions interfere by chemical interaction. Chloride will form a precipitate at the oxidation step. Phosphate and sulfate up to 5 mmoles/50 mL can be tolerated; the absorbances found in the presence of higher concentrations of these anions are rather erratic. As little as 4 mmoles of fluoride interferes, but even at higher concentrations, the addition of sufficient Al serves to complex fluoride and remove the interference. Among cations, Mn interferes by formation of permanganate during the silver oxide oxidation step. The permanganate absorption band causes a slope in the baseline. Uranium does not interfere at concentrations up to 20 g/L.

The standard deviation of the method was found to be 0.007 mg/50 mL for the concentration range from 0.01 to 0.35 mg/50 mL. For the contration range from 0.35 to 7.0 mg/50 mL, the standard deviation varied from 0.01 to 0.137 mg/50 mL, and the relative standard deviation is accordingly between 2.9% and 2.0%.

The preceding method has been recently modified and improved (Ref. 322). Neodymium nitrate is added as an internal standard. Plutonium is again oxidized to the hexavalent state with silver (II) oxide. The excess oxidant is destroyed with sulfamic acid, and the nitric acid concentration is adjusted to 3*M*. The volume is made up to 20 mL. The ratio of the heights of the plutonium 831-nm peak and the neodymium 793-nm peak is measured spectrophotometrically. The spectrophotometer cells have an optical path of 2 cm. The ratio of peak heights obtained with the sample is compared to the ratio obtained with a Pu standard solution containing exactly the same amount of internal standard as the sample and treated in the same manner.

The modified method (Ref. 322) is in routine use for process control at the Marcoule and LaHague reprocessing plants in France. Highly radioactive samples have been analyzed, and the concentration of Pu spanned the range from a few milligrams per liter to several grams per liter. No separations were required. The most precise results in the absence of the internal standard were obtained for a Pu concentration of 50 to 250 mg/L in the cell. The relative standard deviation ranged from 3% to 0.5%. In the presence of the neodymium internal standard, the method is less sensitive to variations in the nitric acid concentration, and relative standard deviations as low as 0.2% have been attained. Comparisons of results obtained by the internal standard method with isotope dilution mass spectrometry for reprocessing plant input solutions containing from 0.3 to 3.7 g Pu/L showed an average difference of 0.67% for 24 sets of measurements. The authors plan to improve the method by weighing aliquots of solutions and by thermostating the sample compartment of the spectrophotometer. Computer automation of all steps in the procedure is planned.

The Tetrapropylammonium Nitrate Method

In this method, the absorbance of an ion association complex of tetrapropylammonium plutonyl trinitrate is measured at either 502 nm or 807 nm (Refs. 122 and 217). The 502-nm peak is more sensitive (molar absorptivity 65.3), but in the presence of Cr there is spectral interference, and the 807-nm peak must be used.

In the manual method (Ref. 122) Pu is oxidized to the hexavalent state with silver (II) oxide. If the solution contains chloride, potassium permanganate may be used as the oxidant, or the solution may be fumed twice with nitric acid before oxidation with silver oxide. An acid-deficient aluminum nitrate salting solution containing tetrapropylammonium nitrate is added to the sample and the plutonyl complex is extracted into methyl isobutyl ketone (hexone). The organic phase is transferred to a spectrophotometer cell, and the absorbance is measured at 502 nm versus methyl isobutyl ketone. The method is applicable to the range of 2 to 15 mg of Pu contained in 0.5 mL or less of solution. The relative standard deviation was 0.3% at the 12.3 mg level. This method was also applied to the analysis of U-Pu mixtures. Solutions contained from 2 to 12 mg of U and Pu in 0.5 mL or less of solution. Measurements of the absorbance of the U peak at 452 nm, the Pu peak at 502 nm, and the valleys at 459 and 519 nm were required. The relative standard deviation for U was 1.2% and for Pu, 1%.

An automated spectrophotometer with narrow band-pass interference filters was constructed at Los Alamos (Ref. 217) for the determination of Pu and U by the tetrapropylammonium method. The wavelengths of the peaks and valleys were 501.4 and 518.0 nm for the more sensitive Pu peak, 807.0 and 768.0 nm for the less sensitive Pu peak, and 452.5 and 460.0 nm for U.

Before placing the sample tubes in the automated spectrophotometer, the analyst needs only to deliver the sample aliquot and, for Pu determination, add a pellet of AgO. The spectrophotometer adds the reagents, performs the extraction and phase disengagement, measures the absorbance, and calculates and prints out the results.

Some modifications were made in the manual procedure (Ref. 122) to adapt the method to the automated spectrophotometer. For Cr-free U-Pu mixtures, AgO is used as the oxidant, the complexes are extracted into 2-nitropropane, and the Pu absorbance is read at 501.4 nm. For Cr-Pu mixtures, extraction may be with either 2-nitropropane or hexone. Plutonium is measured at 807.0 nm. For U-Pu-Cr mixtures, extraction with hexone and measurement of Pu at 807.0 nm is recommended.

Interferences of diverse ions have been thoroughly investigated (Refs. 95, 217, and 244). In addition to Cr, Th interferes. Thorium is complexed by tetrapropylammonium nitrate and extracts into hexone as an insoluble suspension. The Th complex is soluble in 2-nitropropane, which is recommended as a substitute for hexone. Sulfate and fluoride can be tolerated at levels up to 1.8 mmol and 1.5 mmol, respectively, at U or Pu levels of 8 mg or less. At higher levels of U or Pu, less sulfate or fluoride can be tolerated.

The concentration ranges measured with the automated spectrophotometer were 0.5 to 14 mg of Pu and 1 to 14 mg of U, contained in 0.5 mL or less of solution. The precision of the measurements is about 0.02 mg standard deviation over the range, corresponding to a relative standard deviation of 2% at the 1-mg level and 0.2% at the 10-mg level.

Other Chromogenic Agents

Two recently developed spectrophotometric methods for determining microgram quantities of Pu are briefly described. The first (Ref. 323) has been used in India for the estimation of Pu in aliquots containing 1 to 15 μg Pu taken from the aqueous Purex process streams. In this method, Pu(IV) is extracted from $1M$ HNO_3 into $0.5M$ thenoyltrifluoracetone in xylene. The organic layer is scrubbed with $0.5M$ perchloric acid to remove traces of U. Plutonium is stripped with $8M$ HNO_3, leaving most interfering metal ions, especially Zr and Fe(III), in the organic layer. Saturated sulfamic acid solution is added to destroy nitrous acid. The Pu in the aqueous medium is complexed with $0.001M$ arsenazo-III, and the absorbance is measured at 670 nm after 15 min. The relative standard deviation for 12 analyses was determined as 1.9% for 2 μg Pu and 0.58% for 10 μg Pu.

The second method (Ref. 324) has also been used for the analysis of solutions encountered in spent fuel reprocessing. Plutonium(IV) is extracted twice from $4M$ HNO_3 into 2 mL of di-*n*-hexyl sulphoxide. A 0.5-mL aliquot of the combined extracts is transferred to a 10-mL flask. To this, 2 mL absolute ethanol, 0.5 mL glacial acetic acid, and 2 mL of a 0.2% [illegible] of xylenol orange are added, and the solution is made up to volume with absolute ethanol. The absorbance is measured at [illegible]35 nm against a reagent blank. Beer's law is obeyed in the concentration range of 1 to 6.5 μg/mL. Thorium and Zr interfere seriously. For evaluation of the accuracy and precision of the method, 4 experiments consisting of 10 separate analyses were performed. Comparison of "Pu taken" with "Pu found" at the 2- to 5-μg/mL level shows relative errors of −1% to +1.9%. The precision ranged from 0.1% to 0.3% RSD.

Survey of Production Facilities

Routine performance data were not available for this method.

Survey of Exchange Programs

This method was not evaluated by the exchange programs.

4.9.6 Alpha Counting

Description of Method

This method is applicable to the determination of Pu in waste solutions of high- or low-radioactivity levels. Alpha emitters other than Pu interfere, and, if the amount is not known or cannot be determined, they must be separated from the Pu. Extraction with TTA separates Pu from other alpha emitters, such as Am, Cm, U, and Np (Ref. 120). The method requires that the specific activity of Pu be known. If the specific activity must be determined solely for this method, other methods, such as isotope dilution mass spectrometry, should be considered.

For the direct method (no separation), an aliquot of the sample is mounted on a counting disk and the gross alpha activity is determined. Interferring alpha emission is determined and the appropriate adjustments are made.

Alternatively, interfering alpha emitters can be removed. Plutonium is reduced to Pu(III) with hydroxylamine hydrochloride, and then quantitatively oxidized to Pu(IV) with sodium nitrate. Pu(IV) is extracted from 0.5- to 1.5*M* nitric acid solution into 0.5*M* TTA in xylene. The organic phase is separated from the aqueous phase and washed with 0.5*M* HNO_3. An aliquot of the organic phase is evaporated on a counting disk, and the activity is determined by alpha counting. If much Zr or Fe is present, Pu is stripped from the organic phase with 10*M* HNO_3, and the activity of the aqueous phase is determined by alpha counting.

Plutonium (IV) forms a chelate complex with TTA, consisting of a Pu atom bonded to four TTA ions. Both the chelating agent and the metal chelate have low solubility in the aqueous phase and can be extracted into an organic solvent, such as xylene. The concentration of acid in the aqueous solution is critical and must be adjusted carefully so that Pu will be extracted quantitatively. Nitric acid concentrations between 0.5 and 1.5*M* are satisfactory. At lower acid concentrations, Pu polymers may form. At higher acid concentrations, the Pu chelate is not stable, and nitrate complexing of Pu(IV) becomes appreciable. Since Pu(III) and Pu(VI) do not extract, it is necessary to quantitatively adjust the valence to Pu(IV). This is accomplished by reducing all Pu to the (III) state with hydroxylamine hydrochloride and then oxidizing the Pu to the (IV) state with sodium nitrate.

Other alpha emitters, such as U, Am, Cm, and Th do not extract into TTA-xylene from 1*M* acid. Neptunium is not extracted if it is oxidized to the (V) state. Zirconium and Fe do extract, but remain in the organic phase when the Pu is stripped with 10*M* HNO_3.

Scope of Applications

This method is applicable to radioactive solutions that require shielding and remote handling equipment. In an analytical procedure compilation (Ref. 326), it was suggested as a procedure for the determination of Pu in irradiated fuel dissolver solutions. It has been supplanted for dissolver solution analysis by the isotope dilution mass spectrometry method. However, it continues to be of use in the determination of Pu in waste solutions, provided the specific activity of the Pu is known.

Summary of Performance

Two applications of the method as described in the literature are discussed in the "Survey of Selected Literature" and presented in Table 4.42. One user facility has described a direct method for determining Pu that does not employ the preliminary extraction procedure. This application is discussed in the "Survey of Production Facilities" and is also presented in Table 4.42.

Table 4.42 Summary of performance: determination of plutonium by alpha counting

Application	Method	Random Error (% RSD)	Source[a]
Dissolver solutions	TTA extraction; count organic phase	3 to 5	L
	TTA extraction; back extract HNO_3; count aqueous phase	0.8	L
^{239}Pu solutions, 3 to 75 g/L	Direct, 2 π gas proportional	1.8	U
^{239}Pu solutions, 85% ^{238}Pu	Direct, 2 π gas proportional	2.5	U
U-Pu solution, 400 g U/L, 0.4 g ^{239}Pu/L.	Direct, 2 π gas proportional	1.8	U

[a] L = literature survey; U = users' survey of production facilities.
TTA = thenoyltrifluoroacetone

Equipment

Alpha Counter

A number of different types are satisfactory. Desired criteria are stability of the electronic system, capacity to handle high count rates reliably, and tolerance of high beta activity. An alpha counter that employs a silicon surface barrier detector would consist of (1) an evacuable light-tight chamber in which the detector and the counting plate on its support can be mounted, (2) detector bias supply, (3) preamplifier, (4) amplifier with discriminator or single-channel analyzer, and (5) counter and timer.

Counting Disks

Counting disks of stainless steel, preferably with electropolished surface, are recommended to fit the surface barrier detector counting chamber.

Major Sources of Error

The errors most commonly encountered result from several causes:

(1) The counting statistics
(2) Nonquantitative recovery of the Pu from extraction procedure
(3) Self-absorption that occurs if the sample to be evaporated on the counting plate contains nonvolatile impurities that prevent obtaining a "weightless" source. In this case, more accurate results may be obtained by back-extraction of the organic phase with 10*M* nitric acid and electroplating Pu from the aqueous phase onto the counting plate (Refs. 327 and 328). Vacuum sublimation from a hot filament may also be used (Ref. 329).

Known interferences in the method (Ref. 120) are free sulfate, phosphate, fluoride, and oxalate ions. Free sulfuric acid should be maintained at less than 0.1 *N*. Any fluoride ion present in samples must be complexed with aluminum nitrate before Pu is extracted from aqueous nitric acid solutions.

To prevent polymer formation, any dilutions of the sample should be made with at least 1*M* HNO_3.

Measurement Control Requirements

Calibrate the alpha counter using a standard plutonium source having a known activity in terms of disintegrations per minute. Count the known Pu source, and calculate an efficiency factor E as follows:

$$E = \frac{\text{obtained counts/min}}{\text{known dis/min}}$$

Prepare a synthetic sample using a standard Pu solution. This solution may be obtained by dilution of a more concentrated Pu standard solution that has been standardized by a precise titrimetric method. Process an aliquot of the sample through the entire procedure. Calculate a recovery factor R as follows:

$$R = \frac{\text{plutonium determined}}{\text{known plutonium}}$$

An independent measurement control program that evaluates the performance of the counter is essential. It is recommended that routine evaluations of the counter precision and accuracy be carried out on a schedule based on counter use. Suitable quality assurance procedures have been published (Refs. 330 and 331) and are the subject of a proposed ANSI standard (N15.36).

Data Analysis Requirements

Calculate the specific activity of the Pu in the sample as follows:

$$S_t = W_8S_8 + W_9S_9 + W_0S_0 + W_1S_1 + W_2S_2 \qquad (4\text{–}45)$$

where

S_t = total specific activity of plutonium in the sample in (dis/min)/μg

$W_{(8,9,0,1 \text{ and } 2)}$ = weight fraction of the plutonium isotopes 238, 239, 240, 241, and 242, respectively

$S_{(8,9,0,1 \text{ and } 2)}$ = specific alpha activity of the plutonium isotopes in (dis/min)/μg

The specific alpha activity of a nuclide may be calculated from its alpha half-life by the formula

$$\text{sp. act. } [(\text{dis/min})/\mu\text{g}] = \frac{7.93656 \times 10^{11}}{At_{1/2}} \qquad (4\text{-}46)$$

where

A = atomic weight of the nuclide

$t_{1/2}$ = half-life, y

The weight fraction and/or specific alpha activities of some isotopes may make it possible to omit some terms in Eq. 4–45 because they will be negligible.

The amount of plutonium per sample aliquot can be calculated as follows:

$$\text{Pu} = \frac{CF}{S_tVER} \qquad (4\text{–}47)$$

where

Pu = plutonium, μg/mL of sample

C = alpha activity of counting disk, counts/min

F = dilution factor

S_t = total specific activity of the plutonium, (dis/min)/μg (as calculated in Eq. 4–45)

V = volume of diluted sample aliquot, mL

E = efficiency factor of the alpha counter

R = recovery factor

Survey of Selected Literature

Tests performed on dissolver solutions from chemical reprocessing plants indicated that a relative standard deviation of 3% to 5% for a single determination was obtainable for the TTA extraction method when the organic phase was counted. Studies of the back-extraction technique with 10*M* nitric acid on synthetic dissolver solutions (to eliminate Fe and Zr) demonstrated a relative standard deviation of 0.8% for a single determination (Ref. 326). Plutonium recovery, based on tests with standard solutions, was found to be greater than 99.5%.

An interlaboratory evaluation of the same method showed a relative standard deviation between laboratory averages of 6.3%. The relative average laboratory difference from the prepared value of the standard used to evaluate the method was found to be +2% ± 16% (95% confidence limits) (Ref. 152).

Survey of Production Facilities

One facility has applied the gross alpha counting method to a series of control standards prepared to represent different irradiated process solutions. The standards are prepared without the fission products. In this method the solution is diluted and an aliquot of 2.5×10^4 to 5.0×10^4 counts/min is placed on a stainless steel planchet. The solution is dried, fired, covered with a collodion solution, and counted in a 2π methane flow proportional counter for 4 to 10 min.

Solutions containing U and Np are also counted directly without a preliminary extraction. Total counts, however, must be corrected for these alpha emitters from their known concentrations as determined by other methods. In process solutions, the concentration of these alpha emitters is controlled sufficiently that an analysis is not required each time a sample is taken for Pu determination.

The alpha counter is calibrated (counting efficiency determined) by measuring four electrodeposited Pu standard slides every 8 h. Calibration is verified periodically by analyzing control standards at a rate of approximately 20 measurements per month per standard.

The random errors of the method as applied to the different control standards are as follows:

Material	Random Error (% RSD)
^{239}Pu solution, 3 g/L	1.5
^{239}Pu solution, 75 g/L	2.0
^{238}Pu solution, 0.3 g/L	2.5
^{238}Pu solution, 85% ^{238}Pu, 0.04 g/L, with 3.5 g Np/L	2.9
Uranium solution, 400 g U/L, with 0.4 g ^{239}Pu/L	1.8

Survey of Exchange Programs

No exchange data were available for this method.

4.10 DETERMINATION OF PLUTONIUM ISOTOPIC ABUNDANCE

4.10.1 Surface-Ionization Mass Spectrometry

Description of Method

The preferred and most widely used technique for the determination of the isotopic composition of Pu is surface-ionization mass spectrometry. If the abundance of ^{238}Pu is less than 0.7%, alpha spectrometry is frequently used for the determination of that isotope.

In general, mass spectrometry is applicable to the isotopic analysis of Pu in a variety of forms and in mixtures with U. The sample must be dissolved in a suitable acid medium and chemically treated to obtain a purified Pu fraction. The separation of U and Am from Pu is especially important, since ^{238}U and ^{241}Am are mass interferences. A suggested separation scheme is shown in Figure 4.14. The purified Pu fraction (after dilution, if necessary) is used for mass spectrometry. The separation should be used on Pu standards, as well as samples, to remove Am and other decay products. A detailed procedure for the separation and mass spectrometry is given in Reference 332.

An aliquot of the Pu fraction is evaporated on the mass spectrometer filament. A current is passed through to form adherent Pu oxide, and to remove acid, water, and some organic matter. The filament assembly is placed within the ion source of the mass spectrometer and outgassed. The filament(s) are heated following a carefully selected heating pattern to vaporize and ionize Pu. The singly charged metal ions produced by this thermal ionization are accelerated and focused with an electrostatic ion lens into the mass-analyzer section. The total ion beam is separated according to the mass-to-charge ratio of the ions (m/e). By an appropriate variation of the magnetic field(s) or the accelerating potential or both, the separated ion beams are sequentially focused on the detector, which is either a Faraday cup, an electron multiplier, or a photomultiplier detector. The detector current or pulses are further amplified and recorded as a function of the mass on a stripchart recorder or by a digital recording system. The peak currents (intensities) at each isotopic mass are measured, and the average isotopic ratios are calculated with reference to the ^{239}Pu peak intensity. These ratios are corrected for nonlinearities in the detector/recording system and for the mass discrimination of the mass spectrometer. From the corrected isotopic abundance ratios, the isotopic composition of Pu is calculated in atom and weight percent. Alternatively, rather than compute isotope ratios, one may correct the measured intensities for nonlinearities and mass discrimination and then normalize all intensities. The amount of Pu required on the filament for an analysis is 10^{-9} to 10^{-6} g, depending on the sensitivity of the mass spectrometer.

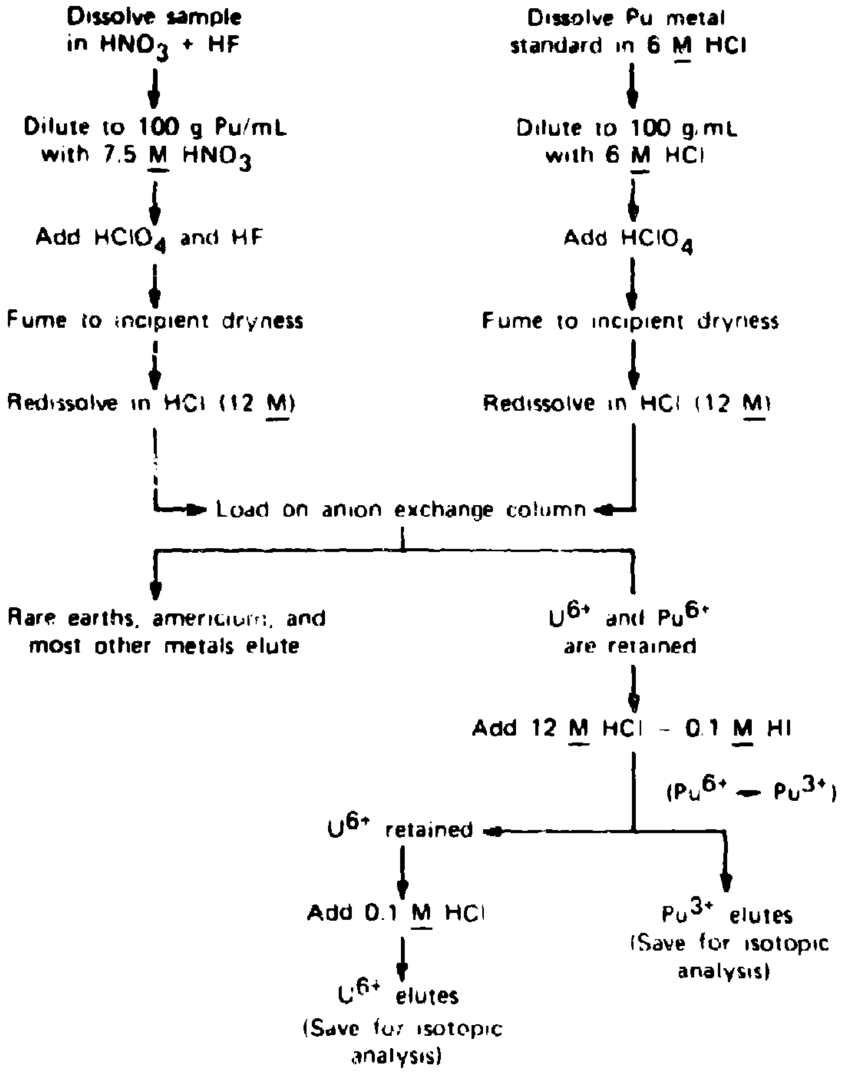

Figure 4.14 Chemical pretreatment steps for plutonium sample and standard solutions.

Variations of this procedure, in which Pu and U are separated together and are sequentially analyzed by increasing the filament temperature, have been proposed (Refs. 333 and 334). In the "resin bead method," developed at Oak Ridge National Laboratory, Pu and U are adsorbed on anion exchange resin beads (Refs. 335 through 337). A single resin bead is loaded into the mass spectrometer. Plutonium and U are analyzed sequentially at different filament temperatures. The normal temperature for Pu analysis is 1450°C to 1500°C. At the completion of the Pu analysis, the temperature is slowly raised to burn off excess Pu. Since U vaporizes at the same time, in order to avoid fractionation of U, care must be taken that this step does not take more than 15 min. Uranium is then analyzed at 1700°C to 1800°C.

Scope of Applications

The method is applicable to a variety of physical and chemical forms of Pu ranging from high-purity plutonium dioxide to spent fuel dissolver solutions. However, spent fuel dissolver solutions are more commonly analyzed by isotope dilution mass spectrometry since the Pu concentration as well as the Pu isotopic abundances is desired. The solution to be analyzed contains the high-purity Pu fraction separated from the dissolution of Pu metal and alloys, Pu oxide, mixed U-Pu oxides, and fabricated Pu-containing nuclear fuels.

The resin-bead technique (Refs. 335 through 337) is especially useful for the isotopic analysis of Pu and U in highly radioactive spent fuel solutions. The technique is recommended for situations in which samples must be shipped for some distance. The beads can be packaged and shipped without the need for shielding. For routine process control and accountability analysis within a plant, the analytical scheme outlined in Figure 4.14 is probably more useful. The resin-bead technique requires 20 to 30 h of equilibration of the solution with the resin.

Summary of Performance

Table 4.43 summarizes the performance of the method as applied to different materials found at production facilities, in exchange programs, and listed in the literature. Where appropriate, the unweighted averages of the performances of different laboratories for similar materials are listed, and the range is given. More details of the specific applications can be found later in this section.

Equipment

Mass Spectrometer

A typical thermal-ionization spectrometer would have a 30.5-cm (12-in.) radius of curvature, 60° or 90° sector, and single or double focusing.

Minimum specifications for such a mass spectrometer are as follows:

(1) Ion source
  (*a*) Thermal-ionization source with triple filament assembly. A single, V-shaped filament is acceptable with an ion-counting detection system.

(*b*) Filament current supply stabilization of one part in 10^4 or better.
(*c*) Pyrex or quartz filament viewing window.

(2) Mass analyzer
(*a*) Mass resolution of 600 at mass 239, or better.
(*b*) Abundance sensitivity of at least 20,000 at a resolution of 600 and a pressure of less than 5×10^{-8} torr in the analyzer (flight tube). Abundance sensitivity is measured at mass positions 238 and 237 on a spectrum generated from natural U.

(3) Vacuum
(*a*) Minimum vacuum of 5×10^{-8} torr in the analyzer and 1×10^{-7} torr in the ion source chamber.
(*b*) Pumping speed sufficient to maintain a vacuum of better than 5×10^{-8} torr during analysis while filament(s) is hot.

Table 4.43 Summary of performance: surface-ionization mass spectrometric determination of plutonium isotopics

Application	Performance (% RSD)		Source[a]
	Random Error	Systematic Error	
PuO_2 powder:			
1.5% ^{241}Pu	0.91 (0.52 to 1.4)	—	E
86% ^{239}Pu	0.024 (0.012 to 0.038)	—	E
Pu metal:			
0.01% ^{238}Pu	20	—	U
93.8% ^{239}Pu	0.10	—	U
5.8% ^{240}Pu	0.[illegible]5	—	U
0.3% ^{241}Pu	0.81	—	U
0.03% ^{242}Pu	7.1	—	U
$(Pu,U)O_2$ powder:			
88% ^{239}Pu	0.031[b]	0.01	U
1.7% ^{241}Pu	0.83	—	E
86% ^{239}Pu	0.047	—	E
$(Pu,U)O_2$ pellets:			
1.7% ^{241}Pu	0.78	—	E
86% ^{239}Pu	0.064	—	E
$Pu(NO_3)_4$ solutions:			
0.001% to 100% isotope	5 to 0.05	—	L
83% ^{239}Pu	0.070 (0.013 to 0.14)	—	E
1.3% ^{241}Pu	0.61 (0.30 to 1.0)	—	E
0.00012 to 0.23 atom ratio ($^xPu/^{239}Pu$)	3.8 to 0.054	—	E

[a] E = survey of exchange programs; L = literature survey; U = users' survey of production facilities.
[b] Includes sampling error.

(*c*) Differential pumping of ion source chamber and analyzer with isolation valve (beam valve) between ion source chamber and analyzer.
(*d*) Vacuum lock sample insertion with sample carriage or multiple-source holder system.

(4) Detection System
(*a*) Overall instrumental sensitivity of 1 × 10^{-9} A s/μg or better; i.e., peak intensity for ^{239}Pu isotope of at least 1 × 10^{-13} A (measured at input to electron multiplier) for an average duration of 1000 s for a filament loading of 0.1 μg of Pu with specified gain and 1-s time constant.
(*b*) Electron multiplier primary detector with stable current gain of 10^5, or, equivalent scintillation photomultiplier tube. Electron multiplier operating mode—either pulse counting or dc current (integrating).
(*c*) Data logging system according to user preference but should include oscilloscope or stripchart recorder to view peaks when tuning spectrometer.

Mass Spectrometer Accessories

(1) Filament material, high-purity, electron beam zone-refined rhenium, tungsten, or tantalum
(2) Filament-forming jig
(3) Filament assemblies (hats)
(4) Spotwelder
(5) Filament-loading unit
(6) Filament bakeout chamber, capable of heating to 2000°C under vacuum of less than 1 × 10^{-6} torr for outgassing of filament
(7) Optical pyrometer, range to at least 2500°C

Other Equipment

(1) Ion-exchange columns: 4- to 6-mm inside diameter, 4- to 6-cm long with drip tip at the bottom and 2- to 3-mL reservoir on top.
(2) Quartz distillation apparatus for distilling water and acids.
(3) Perchloric acid scrubber. The anion-exchange separation procedure (Refs. 119 and 332) calls for oxidation of Pu to Pu(VI) with perchloric acid. It has been shown that a highly efficient perchloric acid fume system (see Figure 4.15) permits one to work safely with perchloric acid in gloveboxes (Ref. 338).

Cost

Surface-ionization instruments with a single-stage magnetic analyzer, Faraday cup, and/or electron-multiplier detector and stripchart recorder can be purchased for approximately $100,000, depending on accessories. Automation systems for peak stepping and digital data acquisition and reduction are about $25,000 to $40,000. Tandem magnetic-analyzer instruments employing pulse-counting detection with automated mass-scanning provisions and digital data acquisition and reduction are priced at about $150,000. Accessories such as gloveboxes, auxiliary vacuum systems, and clean benches can add another $10,000 to $50,000 to the cost of the mass-spectrometric facility.

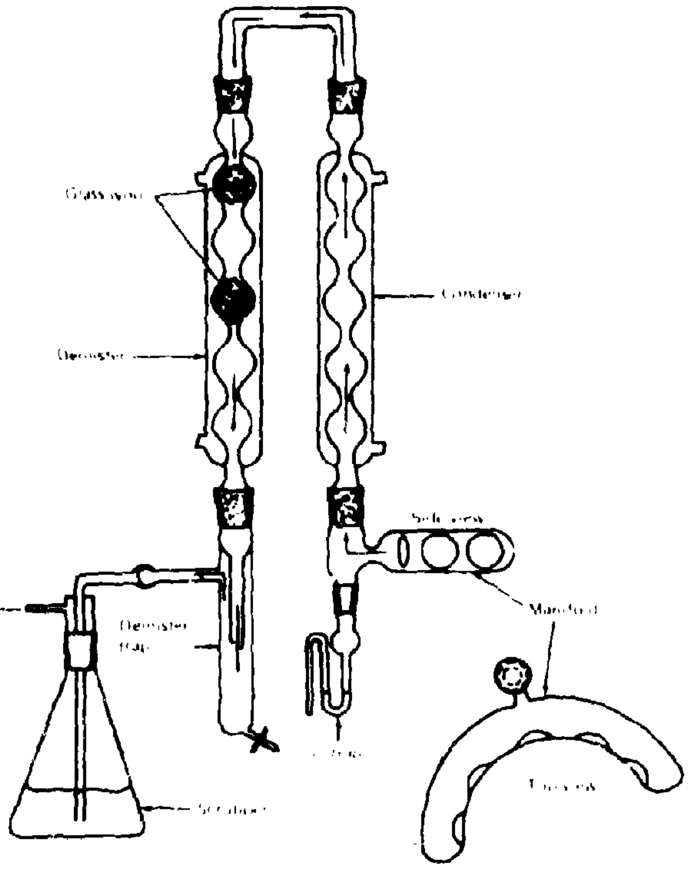

Figure 4.15 Highly efficient perchloric acid fume system. For a detailed description, see Reference 338.

Major Sources of Error

A detailed discussion of sources of error and interferences is given in Ref. 332. Here only an abbreviated account of the principal factors that need to be considered is given.

Source Discrimination (or Source Fractionation)

Thermally produced ions of the lighter isotopes are vaporized and ionized preferentially with respect to the heavier isotopes of the same element. Fractionation is a complex, time-dependent phenomenon. A reproducible analytical procedure must be strictly followed. Such a procedure will keep under control such factors as filament temperature, filament loading, acidity of the sample, chemical form and oxidation state of the element, sample mounting procedure, outgassing procedure, and heating pattern and temperature (Refs. 142 and 259).

Ion-Optical Discrimination

The ion lens and the magnetic sector mass analyzer are not perfect. As a result, the ion path from the exit slit of the ion source to the entry slit of the ion collector/detector is not exactly the same for all ions of a given m/e. To minimize this effect, a high accelerating potential and a large ion-transmission coefficient are desirable (Ref. 260). Again it is necessary to reproduce the spectrometer operating conditions for sample and standard, or for successive filament loadings of the same sample. This includes the mechanical alignment of the filament assembly in the ion source, focus of the ion lens, scanning mode, and scanning rate.

Electron-Multiplier Discrimination and Nonlinearities in the Ion-Current Amplification and Recording System

The procedures given in Reference 332 contain calibration procedures to correct the measurements for these sources of error. Corrections for source, ion-optical, and electron multiplier discriminations have been combined with establishing the mass discrimination factor. This factor is determined using NBS U standards, principally U-500. It is recommended that the mass discrimination factor be verified by also analyzing one of the Pu isotopic standards available from NBS.

Interferences

The accurate mass spectrometry determination of the isotopic composition of Pu depends on the absence of ions with the same nominal mass as the measured Pu ions. The principal interferences are ^{238}U and ^{241}Am. These interferences are removed with high separation factors by an ion-exchange (Ref. 119) or extraction (Ref. 339) procedure.

Significant errors may be introduced into the results unless great care is exercised to prevent sample-to-sample contamination during chemical pretreatment and preparation. Also, U can be a common environmental contaminant in nuclear laboratories. Therefore, scrupulous housekeeping in the working areas is absolutely essential.

The filament material, all reagents, and reagent storage containers should have low levels of U since it may contribute to the instrument background at the U isotopic mass positions. It is recommended that the background of the instrument system be obtained when a new batch of reagents or filament material is used. If the background is unacceptably high, purer filament materials and/or reagents should be obtained.

Interferences may also be caused by source memory. Memory effects are due to the deposition of material on the focusing plates and the ion-source slits. Some of the surface deposits are sputtered off during the analysis of the next sample and are ionized and mass analyzed along with the sample. If the instrument is used for the isotopic analysis of U and Pu samples the existence of a memory effect from the normally intense ^{238}U peak should be checked. If feasible, U and Pu samples should be analyzed on separate instruments or at least at different times using two sources, one for Pu samples and one for U samples. With certain ion source designs, meaningful measurements of ^{238}Pu may not be obtained after a U analysis unless the first source slits (nearest to the filament) are removed and cleaned. Furthermore, U is frequently present as an environmental contaminant that is difficult to remove completely. For these reasons it is recommended that ^{238}Pu be determined by α-pulse-height analysis when its abundance is less than 0.7 weight percent.

Measurement Control Requirements

It is recommended that a primary Pu standard closely approximating the isotopic composition of interest (such as NBS 946) be analyzed each day when Pu samples are analyzed. Control charts for the average value for each isotopic ratio and for the range of these ratios from each filament loading should be established. When the average value of the ^{240}Pu/^{239}Pu ratio changes at the 0.05 significance level, the cause(s) for such shifts should be investigated before continuing with the analysis of samples. It is recommended that a second NBS standard be run immediately after an "out-of-limit" situation arises. This eliminates operator error as a possible cause for the problem.

Data Analysis Requirements

Raw isotopic data, normally obtained from a digital or stripchart recording system, must be corrected for nonlinearities in the detector/recording system and for the mass discrimination of the mass spectrometer. From the corrected isotopic (peak) intensities, Pu isotopic composition may be calculated as atom percent, weight percent, or as a ratio of one isotope to the ^{239}Pu (major) isotope. The calculations are relatively straightforward and can be performed on a desk top calculator. A computer would be recommended, however, for large numbers of analyses. Detailed procedures for calculating isotopic compositions may be found in References 34, 142, 261, 262, 263, and 332.

Survey of Selected Literature

Surface-ionization mass spectrometry is applicable to the determination of the isotopic composition of Pu in any of its forms. The method is absolute to the extent that the mass discrimination factor can be determined with appropriate isotopic standards.

The precision attainable varies with the relative abundances of each isotope. The following approximate relative standard deviations may be expected (Ref. 340) in the isotopic analysis of Pu:

Relative Abundance (weight %)	Randon Error (% RSD)
0.001 - 0.01	5
0.01 - 0.1	3
0.1 - 1	0.2
1 - 10	0.1
10 - 100	0.05

In mass spectrometry, isotopic ratios are measured. Sometimes, ^{239}Pu is used as the reference isotope, as in the method described in this section. Others prefer to use ^{240}Pu as the reference isotope (Ref. 339).

The latest revision of the American Society for Testing and Materials standard methods for mass spectrometry of Pu (Ref. 339) states that isotopic ratios can be measured with the precisions given in Table 4.44 under two sets of laboratory conditions. These precision statements are also based in part upon experience in analyzing isotopic ratios when the average Pu ion current intensity is 1 to 2×10^{-11} A.

The accuracy of an isotope ratio measurement was estimated (Ref. 339) under ideal conditions, where synthetic calibration mixes were prepared from high purity separated isotopes. Three factors are involved in the estimate: mass spectrometric analytical error (precision of the ratio measurement), possible systematic error in the composition of separated isotopes, and possible systematic error in chemical analysis. Under these conditions and with the most favorable isotopic ratio of unity, the accuracy will normally fall between 0.03% and 0.07%, relative. For the ratio range 1 to 20, the accuracy is estimated to be within 0.15%, relative.

Table 4.44 Typical performance for determining plutonium isotopic ratios by surface ionization mass spectrometry[a]

Ratio	% RSD for High-Precision Conditions	% RSD for Production Conditions
1	0.01	0.025 to 0.1
100	0.05 to 0.1	0.1 to 0.25
200	0.15 to 0.25	0.25 to 0.5
500	0.25 to 0.5	0.5 to 1.5
1000	1 to 2	2.5 to 5

[a] From Ref. 339.

The resin bead method has been recommended for safeguards analyses in situations where samples must be shipped some distance. Development of the technique was primarily done on multistage instruments, but a single-stage mass spectrometer has also been used successfully (Ref. 341). Due to the small amount of material adsorbed on the resin bead, the mass spectrometer must be equipped with a pulse-counting detection system. Generally, from 1 to 3 ng of Pu and U were on each bead. Satisfactory analyses of the isotopic composition of both elements can be obtained when the initial dissolver solution has a U/Pu ratio in the range of 50 to 300. There may be problems in accurate determination of ^{238}Pu in the presence of U. A detailed evaluation of the precision of the resin-bead technique was made (Ref. 342) with NBS isotopic standards as samples. The indicated precision was 0.5% RSD for minor isotopes in the 1% concentration range and 0.1% RSD for major isotopes in the 50% range.

Survey of Production Facilities

Several production facilities use surface-ionization mass spectrometry for Pu isotopic analysis, and, among these, two had routine performance data available.

In the first application, for Pu metal, a preliminary ion exchange separation is performed to remove ^{241}Am. A double filament, single focusing mass spectrometer with direct-current detection and automatic data acquisition and calculation is used to analyze a 5-μg aliquot of the purified sample. The mass discrimination calibration factor is determined by analyzing three NBS U-500 standards per week. The calibration is verified by analyzing a Pu metal control standard at the same frequency.

The random error of the method as applied to Pu metal and at the levels indicated is as follows:

Relative Abundance	Random Error (% RSD)
0.01% ^{238}Pu	20
93.8% ^{239}Pu	0.10
5.8% ^{240}Pu	0.26
0.3% ^{241}Pu	0.81
0.03% ^{242}Pu	7.1

The second application, for Pu-U mixed oxide, employs a high-precision double focusing mass spectrometer with direct-current detection and automatic data acquisition and calculation. The sample undergoes a double ion exchange procedure to remove ^{241}Am and U isotopes. The mass discrimination factor is determined periodically by analyzing NBS U-500, and the calibration is verified by analyzing blind control standards.

The random error of the method for ^{239}Pu is 0.031% RSD for $(Pu,U)O_2$ at the 88% ^{239}Pu level. A systematic error of 0.01% RSD was determined by statistically combining the random error of the mean of the control standard determinations and the total uncertainty of that standards certified value.

Survey of Exchange Programs

In the SALE (Ref. 154) program, surface-ionization mass spectrometry has been applied to a number of materials for determining ^{239}Pu and ^{241}Pu isotopic compositions. Specific methods as applied by the different laboratories were not defined. Table 4.45 presents the within-oratory random errors for the method as applied to the listed materials.

le 4.45 Surface-ionization mass spectrometric determination of plutonium isotopics—SALE exchange program

	^{239}Pu		^{241}Pu	
Application	Abundance (%)	RSD (%)	Abundance (%)	RSD (%)
PuO_2 powder	86	0.038	1.5	0.62
		0.012		1.4
		0.025		0.52
		0.019		1.1
$(Pu,U)O_2$ powder	86	0.067	1.7	1.3
		0.026		0.38
$(Pu,U)O_2$ pellets	86	0.064	1.7	0.78
$Pu(NO_3)_4$	83	0.14	1.3	0.78
		0.090		1.0
		0.036		0.30
		0.013		0.37

The plutonium isotope sample exchange program (R. L. Carpenter, Rocky Flats Plant, unpublished information, Aug. 1980-Jan. 1981) incorporates mass spectrometry to determine plutonium isotopic ratios on one oxide and five nitrate materials. After preliminary separation of ^{241}Am (solvent extraction or ion exchange), three filament loadings are prepared and run for each sample. No specific method details are reported. Figure 4.16 presents the method performance of six participating laboratories for the six different exchange materials. Random error is plotted versus atom ratios of the specific Pu isotopes (^{238}Pu, ^{240}Pu, ^{241}Pu, and ^{242}Pu) to the ^{239}Pu isotope. Each curve is defined by the four ratios associated with each of the six exchange samples (24 points per curve). The six-laboratory mean shows that random errors of 0.054% to 3.8% RSD can be expected for the method at atom ratios ranging from 0.25 down to 0.00012. No significant variation is seen in the performance of the method due to different material types.

4.10.2 Alpha Spectrometry

Description of Method

It is frequently desirable to determine the isotopic abundance of ^{238}Pu by a method other than mass spectrometry. This is especially the case for samples where ^{238}Pu content is too low for precise mass spectrometric measurement, or where there is interference from ^{238}U either as background in the mass spectrometer or as contamination of the sample. Alpha spectrometry has been reported as the method of choice for the determination of ^{238}Pu isotopic abundances from 0.01 to 0.7 weight percent (Refs. 343 and 344). Mass spectrometry should be used for the measurement of higher abundances, but can be used for ^{238}Pu abundances as low as 0.1 weight percent, depending on the mass spectrometer, the amount of sample used, and the degree of decontamination from ^{238}U achieved by the preliminary chemical separation.

Alpha spectrometry is particularly suited for the determination of ^{238}Pu because of the high specific alpha activity of that isotope relative to the other alpha-active Pu isotopes. For instance, in a Pu sample containing 0.15% ^{238}Pu, 86% ^{239}Pu, and 11.5% ^{240}Pu, nearly 25% of the total alpha activity is contributed by ^{238}Pu. In computing the total alpha activity, only the above isotopes need to be considered. The specific alpha activities of ^{241}Pu and ^{242}Pu are too low to make a significant contribution, and may be safely neglected even at isotopic abundances of 10 weight percent each. The energies of the alpha particles emitted by these two isotopes are outside the energy region of the measurement. The ^{238}Pu alpha peaks at 5.50 and 5.46 MeV are well resolved from the group of ^{239}Pu and ^{240}Pu alpha peaks in the region of 5.11 to 5.17 MeV. The group of ^{293}Pu and ^{240}Pu alpha peaks cannot be resolved from each other. Spectra of each isotope, taken at high resolution, can be found in Reference 345. Table 4.46 lists the principal alpha peaks of the isotopes of interest.

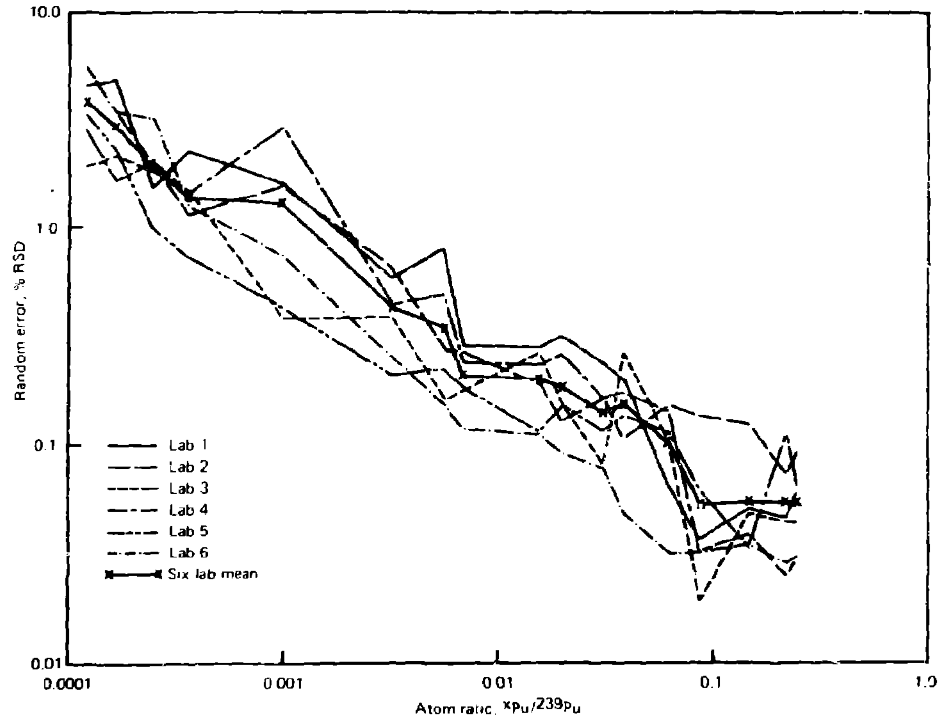

Figure 4.16 Surface-ionization mass spectrometry—plutonium isotopic sample exchange program performance.

Table 4.46 Principle alpha peaks of interest[a]

Nuclide	$t_{1/2}$, yr	Alpha-Particle Energy (MeV)	Alpha-Particle Abundance (%)
^{238}Pu	87.74	5.499	72
		5.456	28
^{239}Pu	24,119	5.157	73.3
		5.145	15.1
		5.107	11.5
^{240}Pu	6,537	5.168	76
		5.123	24
^{241}Am	432.5	5.486	86
		5.443	12.7
		5.389	1.3

[a] Data taken from Ref. 345. Half-lives have been updated to values currently accepted (Ref. 32). Peaks of low abundance (less than 0.1%) have been omitted.

A portion of a suitable dissolution of the Pu-bearing material is diluted with 1*M* nitric acid. An aliquot of the dilute solution is extracted with an equal volume of 0.5*M* TTA in xylene. An aliquot of the organic phase is evaporated on a counting disk. Alternatively, the Pu fraction may be separated and purified by an ion-exchange procedure. In that case, an aliquot of the purified Pu fraction is evaporated on a counting disk. Preparation of a "weightless" uniformly distributed sample is essential to optimal performance. The presence of inert residue can lead to alpha absorption and a degraded alpha spectrum. The recommended procedure involving plating of an organic phase extractant and subsequent flaming of the counting plate has provided good results. The alpha spectrum in the 5 to 6-MeV region is measured, using a silicon surface-barrier detector with associated electronics and a multichannel pulse-height analyzer. The total counts in the ^{238}Pu and (^{239}Pu + ^{240}Pu) peaks are obtained and corrected for background. The ^{238}Pu abundance is calculated from the ratio of the alpha activity due to ^{238}Pu to the total alpha activity, and the abundance of ^{239}Pu and ^{240}Pu determined by mass spectrometry on a separate portion of the sample. A single determination requires only a few minutes for source preparation (beginning with a purified Pu fraction) and approximately 10 min of counting time. A detailed procedure may be found in Reference 346.

Scope of Applications

This method is applicable to Pu-bearing materials that have a ^{238}Pu abundance that is too low for precise mass spectrometric measurement, or to situations in which there is a significant interference from ^{238}U. Precise measurement of the ^{238}Pu abundance is essential for calorimetric measurements of total Pu since ^{238}Pu contributes a large fraction of the heat. Alpha spectrometry has been reported as the method of choice for the determination of ^{238}Pu isotopic abundances from 0.01 to 0.7 weight percent (Refs. 343 and 344).

Summary of Performance

One application reported in the literature has a random error of 2% RSD or better for ^{238}Pu at the 0.01% level (Ref. 54). Routine user and other literature performance data were not reported. The method was not evaluated in the exchange programs.

Equipment

Alpha Spectrometer

This spectrometer will consist of the following components:

(1) Silicon surface barrier detector, with an active area of 100 mm^2, 100-μm depletion depth, and a resolution of 20 keV or less FWHM (for ^{241}Am, 5.486 MeV alphas) is suitable. A detector with a rear microdot connector should be specified.

(2) Evacuable light-tight chamber in which the detector and the counting plate on its support can be mounted. Surface-barrier detectors may be operated at atmospheric pressure. However, the inelastic scattering of alpha particles by air decreases the resolution. It is recommended that the chamber be evacuated with a roughing pump to 1×10^{-2} to 5×10^{-2} torr. The roughing pump should have a suitable trap between it and the chamber to prevent the back-streaming of pump oil. There should also be an interlock that prevents application of the bias voltage to the detector until the chamber has been evacuated. The alpha spectrometer should be operated in an environment in which both temperature and humidity are controlled.

(3) Preamplifier, charge-sensitive field effect transistor (FET), with noise less than 4.6 keV when used with the silicon surface barrier detector (100-pf capacitance).

(4) Detector bias supply, 0 to 1000 V, continuously variable, well regulated and stable.

(5) Main spectroscopy amplifier, low noise, with variable shaping constants and baseline restoration.

(6) Biased amplifier and pulse stretcher, with continuously adjustable post gain and automatic pileup rejection.

(7) Multichannel pulse-height analyzer. A 512-channel is most versatile and convenient, since it can be used for the acquisition of data from one to four detectors simultaneously. Even if only one detector is used, such an analyzer has the advantage that

background may be stored in another subgroup and subtracted electronically from the spectrum of interest, and that several spectra can be stored and compared. An analyzer that permits setting windows around the peaks of interest and electronic integration is especially convenient. The analyzer should accept pulses from 0 to 10 V and from 3 to 6 μs in width, and should have a capacity of 10^6 counts full scale per channel.

(8) Teletypewriter, printer, or other peripheral devices may be used for output of the data from the multichannel analyzer.

Counting Disks

Counting disks of highly polished Pt or Ta, 25 mm diameter by 0.051 mm (1-in diameter by 0.002-in.), are suggested. Platinum is preferred. Make a 4-mm diameter depression in the center with a fire-polished glass rod or the round end of a small test tube. Microscope cover slides (25 by 25 by 0.12 mm) have been recommended (Ref. 347). These slides have a smooth polish and are inexpensive and disposable; however, they require care in handling and flaming.

An infrared heat lamp and disposable micropipets are also required equipment.

Major Sources of Error

Errors most commonly encountered result from the following:

(1) The counting statistics
(2) Mass spectrometric determination of the ^{239}Pu and ^{240}Pu abundances
(3) Uncertainties in the half-lives of the Pu isotopes.
(4) Thick or nonuniform deposits on counting disks.

Americium-241, which is always present as a result of the decay of ^{241}Pu, constitutes a direct interference (see Table 4.46) and must be removed prior to the determination of ^{238}Pu. The ion-exchange procedure given in Reference 346 gives a good separation from ^{241}Am, as well as from other nuclides that would interfere with the alpha pulse-height determination, such as ^{232}U, ^{243}Am, ^{245}Cm, and ^{249}Bk. Since an alpha activity ratio is measured in the determination, quantitative recovery of the Pu is not required.

Alpha spectrometry is preferably done within a day of the purification, especially if the abundance of ^{241}Pu is high, since ^{241}Am will grow in again from the beta decay of ^{241}Pu. However, if prompt analysis is not possible, suitable corrections for the bias due to ^{241}Am interference may be made up to a period of several weeks following the purification.

Under normal conditions, if an Am decontamination factor of 300 or better was reached in the ion-exchange separation and if alpha spectrometry is promptly performed after purification, there is no interference.

Measurement Control Requirements

It is recommended that a counting standard (^{238}Pu or ^{241}Am) be analyzed each day that Pu samples are analyzed. Control charts for the average number of counts given by the standard should be established. When the average value changes at the 0.05 significance level, the cause(s) for such shifts should be investigated before continuing with the analysis of samples. It is recommended that a recount be done immediately after an "out-of-limit" situation arises to eliminate technician error as a possible cause for the problem.

An independent measurement control program that evaluates the performance of the multichannel analyzer is essential. It is recommended that routine evaluations of the precision and accuracy be carried out on a schedule based on use of the analyzer. Suitable quality assurance procedures (Refs. 330 and 331) have been published and are the subject of a proposed American National Standards Institute standard (N15.36). The system gain and resolution should be checked periodically to maintain the same operating conditions and to check whether any deterioration of the spectrometer has taken place.

Data Analysis Requirements

The abundance ratio, $R_{8/9} = {}^{238}\text{Pu}/{}^{239}\text{Pu}$, may be calculated as follows:

$$R_{8/9} = \frac{C_8}{C_9}\left(\frac{S_9}{S_8} + \frac{S_0}{S_8}R_{0/9}\right) \qquad (4\text{–}48)$$

where

$R_{8/9}$ = ^{238}Pu/^{239}Pu abundance ratio
$R_{0/9}$ = ^{240}Pu/^{239}Pu average isotopic ratio from mass spectrometry, corrected for mass discrimination
C_8 = observed net counts in the 5.50- and 5.46-MeV peaks, due to ^{238}Pu
C_9 = observed net counts in the 5.11- to 5.17-MeV region, due to ^{239}Pu and ^{240}Pu
S_8 = specific alpha activity of ^{238}Pu = 3.800×10^7 dis/min/μg
S_9 = specific alpha activity of ^{239}Pu = 1.376×10^5 dis/min/μg
S_0 = specific alpha activity of ^{240}Pu = 5.058×10^5 dis/min/μg

The above formula applies if alpha spectrometry is performed promptly after the removal of ^{241}Am by ion exchange. If more than 2 days elapse between the separation and alpha spectrometry, the 5.50- and 5.46-MeV peaks will contain enough counts due to ^{241}Am, which has grown in from the beta decay of ^{241}Pu, to require a correction. Under these conditions, the measured ratio M may be defined as follows:

$$\frac{C_8 + C_{\mathrm{Am}}}{C_9} = M \qquad (4\text{-}49)$$

where C_{Am} are the counts in the 5.50 and 5.46 MeV peaks due to ^{241}Am. The true abundance ratio ^{238}Pu/^{239}Pu, corrected for ^{241}Am, is equal to

$$R^{*}_{8/9} = \frac{S_9}{S_8}\left[M\left(1 + \frac{S_0}{S_9}R_{0/9}\right) - \frac{S_1}{S_9}R_{1/9}\lambda_{\mathrm{Am}}t\right] \qquad (4\text{-}50)$$

where

$R^{*}_{8/9}$ = ^{238}Pu/^{239}Pu abundance ratio, corrected for ^{241}Am interference
$R_{1/9}$ = ^{241}Pu/^{239}Pu average isotopic ratio from mass spectrometry, corrected for mass discrimination
S_1 = specific beta activity of ^{241}Pu = 2.286×10^8 dis/min/µg
λ_{Am} = decay constant of ^{241}Am = ln 2/half life, expressed in days (432.5 years × 365.2422 days/yr)
t = time elapsed since the ^{241}Am separation, days

The ratio $R_{8/9}$ or $R^{*}_{8/9}$ is then used with the other isotopic ratios obtained by mass spectrometry to calculate the atom percent and weight percent of each isotope. Detailed procedures for calculating atom and weight percents may be found in References 261 and 332.

Survey of Selected Literature

The relative standard deviation of the method is 2% or better, depending on the total integrated counts in each peak. The 2% figure is based on accumulating at least 2500 counts in the ^{238}Pu alpha peak for samples containing 0.01 % of that isotope (Ref. 52). For most samples, a much larger count will be accumulated in this peak, with correspondingly better precision. The inaccuracy with which the half-lives of the Pu isotopes are known constitutes a bias of the method. Data on the ASET-74 Intercomparison Experiment and information on procedures for peak tail correction are given in Reference 343.

Survey of Production Facilities

No routine performance data were available.

Survey of Exchange Programs

Alpha spectrometry was not evaluated in the exchange programs.

4.11 SIMULTANEOUS DETERMINATION OF URANIUM AND PLUTONIUM

4.11.1 Isotope Dilution Mass Spectrometry

Description of Method

Mass spectrometric measurement of elemental concentration may be performed by the method called isotope dilution mass spectrometry. In the nuclear fuel cycle, this measurement method is most frequently applied to determinations of the Pu and U concentrations (and isotopic compositions) in the input accountability tank of fuel reprocessing plants but may, of course, be used elsewhere.

Isotope dilution mass spectrometry (IDMS) (Refs. 333 and 348 through 353) involves addition of a measured quantity of a highly enriched isotope to an aliquot of the sample. The isotope must either not be present or is present only at small relative levels in the sample. The added element of known isotopic composition is termed the "spike." After chemical and isotopic equilibration, the quantities of the isotopes in the sample are measured relative to the added isotope by mass spectrometry. From the change in the isotopic ratios of the sample caused by the spike, the elemental content of the sample may be calculated.

The basic steps in an IDMS procedure are as follows:

(1) Obtain and prepare a representative and accurate aliquot of the sample.

(2) Add accurately known amounts of the spike isotopes to the sample aliquot.

(3) Achieve identical chemical states of the isotopes and isotopic equilibrium between the sample and the spike prior to any chemical separations.

(4) Separate the U and Pu from each other and from fission products and Am.

(5) Carry out the mass spectrometric analysis and subsequent calculations.

For fuels containing natural U, enriched ^{235}U, and Pu, the conventionally used spike isotopes are ^{233}U and ^{242}Pu. With increasing burnup of the fuel and the consequent increased formation of ^{242}Pu in the fuel specimen, this isotope becomes less desirable as a spike. If the abundance of ^{242}Pu in the fuel is 5% to 10%, ^{242}Pu can still be used as a spike isotope, but an unspiked sample must, of course, be analyzed to correct the amount of ^{242}Pu originally present. A preferable spike isotope in this case is ^{244}Pu. For fuels containing ^{233}U, the suggested spike isotope is ^{236}U.

In mass spectrometry, isotope ratios are measured most accurately at a value of unity. The error generally remains less than 0.1% RSD for the range of ratios from 0.3 to 3 for well-tuned and calibrated mass spectrometers. The general rule is to select the sample aliquot so that the ratio of the most important isotope to the spike isotope is within the range of 0.3 to 3. The minimum recommended amount of U in the sample aliquot is the equivalent of 150 μg of ^{238}U, to decrease to insignificant levels the effect of U blanks in chemical reagents, apparatus, and mass spectrometer filaments.

More strenuous conditions are required than are ordinarily believed to be necessary to achieve identical chemical states of the isotopes in the sample aliquot and the added spike. Chemical identity is necessary to insure that all isotopes are recovered equally in the chemical separation. Another need for chemical identity is the fact that the rate of production of ions from a mass spectrometer filament is dependent on the chemical state of the isotope on the filament. Hence, even when chemical separations are not used, for example, the calibration of U spike solutions and the calibration of Pu spike solutions that do not contain significant amounts of ^{241}Am, there is still need for chemical identity.

The mixture of the sample aliquot (or calibration standard) and the spike isotope solution should be subjected to a vigorous chemical reaction or set of reactions to guarantee the chemical identity of all isotopes. IDMS procedures differ in the chemical reactions used to achieve chemical and isotopic equilibration. Various reduction-oxidation cycles that have been used are (1) reduction with hydroxylamine hydrochloride, oxidation with sodium nitrite (Ref. 334); (2) reduction with ferrous ammonium sulfate, oxidation with sodium nitrite (Refs. 350 and 354); (3) oxidation with potassium permanganate (Ref. 10). Such cycles may fail to produce chemical identity in some cases, especially when samples contain complexing agents and polymerized species. A procedure that works well in such cases (Ref. 119) consists of fuming all mixtures with concentrated perchloric acid and 1 to 2 drops of hydrofluoric acid to copious fumes of perchloric acid, stopping just short of dryness. This treatment performs the dual function of placing all isotopes in the (VI) valence state and of dissociating any polymeric species of U and Pu. Two precautions must be observed when using perchloric acid fuming. Any plastic ware used must be tested for reaction with fuming perchloric acid (Teflon and Kynar are satisfactory). Several fission products, notably Ru and Tc, volatilize during the fuming and must be contained to prevent inhalation by personnel. Unless the enclosure in which operations are carried out is specially designed for perchloric acid fuming, use of a perchloric acid scrubber, as shown in Figure 4.15, is desirable.

Several different procedures are used for the separation of U and Pu from each other and from fission products, Am, and other ions. The anion-exchange procedures include adsorption from 7.5 or 8.0*M* HNO_3 (Refs. 350, 352, and 354) or from 10 or 12*M* HCl (Ref. 10, pp. 388-392; Ref. 119). Adsorption from 12*M* HCl can be readily used following the $HClO_4$ fuming, since that anion-exchange procedure (Ref. 119) is based on having both U and Pu in the hexavalent state and in the form of chloride complexes. That procedure provides better decontamination for U and Am than ion-exchange in a HNO_3 medium:

Acid Medium	Decontamination Factors Relative to Pu	
	Am	U
12*M* HCl	300	10^5
7.5*M* HNO_3	140	10^3

The decontamination factor for U in the Pu fraction is amply high to permit the isotopic abundance measurement of ^{238}Pu by mass spectrometry (Ref. 119). (Separation factors for the U fraction when using the 12*M* HCl medium are $>10^4$ for Am and 150 for Pu.) The nitric acid separation does not give a Pu fraction sufficiently free of U to permit the reliable measurement of the ^{238}Pu isotopic abundance by mass spectrometry. Further purification of both the U and Pu fractions is generally required.

Solvent extraction separations that have been used include extraction of Pu into TTA-xylene (Ref. 351) and extraction of U into methyl isobutyl ketone (Ref. 10, pp. 368-373; Ref. 244).

In some procedures, Pu and U are separated together, either by ion-exchange (Ref. 334) or by liquid-liquid extraction (Ref. 333), and are sequentially analyzed by increasing the filament temperature. Prominent among these procedures is the resin bead method, in which Pu and U are sorbed on a few anion-exchange resin beads, and a single resin bead is loaded into the mass spectrometer (Refs. 335, 336, 337, 341, and 342). The sequential analysis scheme is shown in Figure 4.17. Since equilibration of the solution with the resin requires 20 to 30 h, other procedures that involve separation of U from Pu and separate analysis of the two elements are preferable for routine accountability measurements in a plant.

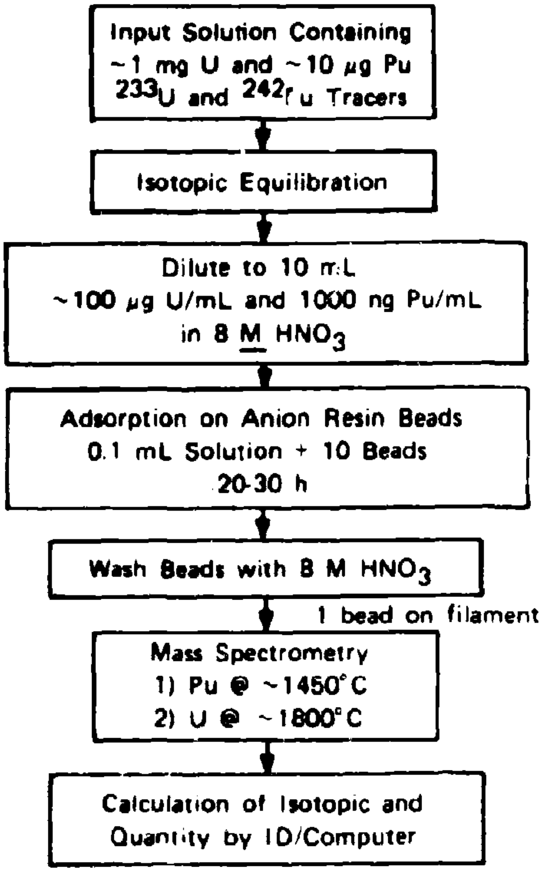

Figure 4.17 Sequential analysis of Pu and U (resin bead method).

The procedure recommended here (Ref. 119) minimizes the preanalysis treatment, achieves chemical and isotopic equilibration of the sample and spike, and gives excellent separation of Pu and U from each other and from diverse ions. In this procedure, an aliquot of the solution to be analyzed is spiked with accurately known amounts of ^{233}U and ^{242}Pu or, preferably, ^{244}Pu. (Plutonium-244 is preferred since high burnup fuel contains sufficient ^{242}Pu to require analysis of an unspiked sample for correction purposes.) A small amount of hydrofluoric acid is added to the sample. The Pu and U ions are brought to a common oxidation state, (VI), by fuming the solution strongly with perchloric acid. Fuming with perchloric acid in the presence of hydrofluoric acid also serves to destroy any Pu polymers that may be present. The dried salts are dissolved in 12*M* hydrochloric acid and the solution is transferred to an ion-exchange column where Pu and U are sorbed as chloride complexes. Plutonium is eluted as Pu(III) with a 12*M* HCl/0.1*M* HI mixture and U, still as U(VI), is eluted with 0.1*M* HCl. The Pu and U fractions are each evaporated to dryness. One mL of concentrated nitric acid and 2 drops of 1*M* perchloric acid are added and evaporated to dryness to destroy organic impurities from the resin. The residues are taken up in 2*M* nitric acid to give U and Pu concentrations appropriate for mass spectrometry. A detailed procedure is given in Reference 31.

The preparation of the sample, including separations, requires about 2 man-hours. Many ion-exchange columns can be operated in parallel to increase sample throughput. Filament preparation, preliminary outgassing in a separate vacuum system, loading the filament, inserting the filament into the mass spectrometer, and obtaining the spectra require about 1 h. The elapsed time may be as high as 4 h if pumping speeds or filament outgassing rates in the instrument are slow. The measurement of recorder charts and manual data reduction requires another 1 to 2 h. If computerized data acquisition and reduction are available, this time is reduced to a few minutes.

With an automated scan capability, a sample-introduction lock, high-speed pumping system, and digital data acquisition and reduction, two operators can process about 12 samples per day. Of course, complex instrumentation systems do not have a 100% run time. In addition to competent spectroscopists, the facility needs well-trained and qualified operators and, very important, adequate electronic and computational support.

Scope of Applications

Isotope dilution mass spectrometry is applicable to the determination of U and Pu concentrations in solutions that result from the dissolution of nuclear reactor fuels. The technique is an adaptation of the mass spectrometric methods for the determination of isotopic abundances that permit measurement of the elemental concentrations. As a result, the technique also provides isotopic abundance data.

The technique is applicable to dissolver solutions of nuclear fuels containing Pu, Al, Zr, or stainless steel. The technique is also applicable to process streams and waste tank solutions. The sample size required for mass spectrometric analysis is 10^{-9} to 10^{-6} g of Pu and 10^{-8} to 10^{-5} g of

U, depending on the sensitivity of the instrument. However, it is recommended that aliquots containing at least 1.5×10^{-4} g of U be carried through the chemical separation.

The resin-bead technique (Refs. 335, 336, 337, 341 and 342) is especially useful for the determination of Pu and U in highly radioactive spent fuel solutions. The technique is recommended for situations in which samples must be shipped from one laboratory to another some distance away. The beads can be packaged and shipped without the need for shielding.

Summary of Performance

No user and exchange data are available. The literature survey, described in some detail in this section, shows that random errors of 0.15% to 1.3% RSD are obtainable for mixed U/Pu solutions, depending generally on whether volumetric or weight sample and spike aliquots are taken. For weight aliquots, 0.15% RSD was obtained for either Pu or U. For volumetric aliquots a random error of 0.6% to 1.3% RSD for U and 0.6% RSD for Pu were obtained (Refs. 152, 351, and 354). Errors of 0.6% RSD for U and 0.9% RSD for Pu were obtained for the resin bead technique (Ref. 342).

Equipment

The sample preparation steps in IDMS require no special laboratory equipment other than a semimicro analytical balance, disposable ion-exchange columns, and perchloric acid scrubber. (See Fig. 4.15.) The mass spectrometer and associated equipment are described in the sections on isotopic analysis by surface-ionization mass spectrometry and in Reference 31.

Major Sources of Error

Errors most commonly encountered result from the following:

(1) Uncertainty in the accuracy of the semimicro analytical balance used for weighing the initial sample, subsequent dilutions, and spike aliquots
(2) Uncertainty in the assay of the spike solutions
(3) Failure to obtain chemical and isotopic equilibrium of sample and spike
(4) Failure to obtain adequate separation of Pu and U
(5) Failure to remove organic impurities from the Pu and U fractions

Sources of error in mass spectrometry are listed in the sections on isotopic analysis by surface-ionization mass spectrometry and are discussed in detail in Reference 31.

Uranium-238 will interfere with the measurement of ^{238}Pu. The recommended ion-exchange separation should remove this interference so the ^{238}Pu can be accurately determined. If the ^{238}Pu isotopic abundance is 0.1% or less, it may be necessary to repeat the purification step, or to determine ^{238}Pu by alpha spectrometry. The presence of ^{238}U in the Pu fraction can be detected by observing the ^{235}U peak. If the ^{235}U peak is 0.1% or more, relative to the ^{238}Pu peak, the Pu fraction must be repurified. The interference of ^{241}Am with the determination of the ^{241}Pu isotope is removed by the recommended separation procedure.

Plutonium-238 will interfere with the measurement of ^{238}U. The recommended separation procedure should remove this interference; however, when the U fraction is analyzed, if the ^{239}Pu peak is 1% or more relative to the ^{238}U peak, the U fraction must be repurified.

Uranium-233 will interfere with the U concentration determination, since ^{233}U is used as a spike isotope. It is not expected that irradiated LWR fuels will contain significant amounts of ^{233}U. However, if the ^{233}U is 0.01% or more relative to the ^{238}U, an unspiked sample must be analyzed as well, to be able to correct for the amount of ^{233}U originally present.

Significant errors may be introduced into the results unless great care is exercised to prevent sample-to-sample contamination during chemical pretreatment and preparation. Also, U can be a common environmental contaminant in nuclear laboratories. Therefore, scrupulous housekeeping in the working areas is absolutely essential.

Measurement Control Requirements

The constancy of the mass discrimination bias factor is monitored by frequent, preferably daily, analysis of an NBS isotopic U standard. A control chart should be maintained. If the value obtained in an analysis of a standard falls outside the 95% confidence interval, the analysis should be rerun. If two consecutive values indicate a bias in the same direction outside the 95% confidence interval, the mass discrimination bias factor should be redetermined. When data indicate the method is out of control or any major changes in the instrument are made, such as changing the ion source or electron multiplier or realigning either the electrostatic or magnetic analyzer, the measurement system must be recalibrated. It is also recommended that a primary Pu reference material closely approximating the isotopic composition of interest be analyzed each day that Pu samples are analyzed.

Data Analysis Requirements

Raw isotopic data, normally obtained from a digital or stripchart recording system, must be corrected for nonlinearities in the detector/recording system and for the mass discrimination of the mass spectrometer. The U or Pu concentration is calculated from the corrected isotopic (peak) intensities of the sample, spike, and sample plus spike solutions, and from the known U or Pu concentration of the spike solution. The calculations are somewhat complicated and are best performed on a computer. Details of the calculations may be found in References 10 and 34.

Survey of Selected Literature

The reliability of the isotope dilution mass spectrometer method has been discussed in detail by Rein and Metz (Ref. 355). They concluded that the precision approaches 0.15% RSD for a single determination when the sample aliquot and spike isotope are added on a weight basis. This is the expected error based on a mass spectrometric measurement of isotope ratios to 0.1% and a weighing error also of 0.1%. With volume deliveries of sample and spike isotope aliquots, this error increases depending on the precision of the pipetting apparatus.

Bokelund (Ref. 351) gave results of the analysis of typical dissolver solutions from the Eurochemic reprocessing plant, under plant conditions. He found the overall precision of the Pu concentration measurement to be 0.6% RSD, including the plant sampling error, dilution error, and analytical error.

In an interlaboratory comparison (Ref. 354) of the measurement of U and Pu concentrations, the within-laboratory relative standard deviation was 0.6% and the between-laboratory relative standard deviation was 0.7%.

In another round robin, seven laboratories determined the U concentration of a solution at the 443 μg/mL level (Ref. 152). The results showed a precision of 1.3% RSD and a bias of −0.2% ± 5.5% (relative difference, ± 95% confidence limit). Improved precision could be obtained by analyzing on a weight basis instead of a volume basis.

The resin bead technique has been reported to give an accuracy of 0.5% relative for the isotope dilution measurement of Pu and U concentrations in synthetic dissolver solutions (Ref. 342). The internal precisions were 0.9% for Pu and 0.6% RSD for U.

Survey of Production Facilities

No routine performance data were available.

Survey of Exchange Programs

No performance data have been reported for this method.

4.11.2 X-Ray Fluorescence Spectrometry

Description of Method

X-ray fluorescence spectrometry (XRF) has been applied to the determination of actinide elements for nearly 30 years. With improvements in the instrumentation, XRF has been used for the analysis of increasingly complex samples. Most of the early applications were for the determination of U in solutions or fusions prepared from U alloys or unirradiated oxide fuel. Subsequently, the technique was extended to the determination of Pu and U, of various ratios, in solution or in unirradiated MOX fuel pellets. Most recently, much work has been done on the determination of Pu and U in highly radioactive reprocessing plant samples.

In X-ray fluorescence spectrometry, atoms within the sample are excited through bombardment with a beam of energetic particles or electromagnetic radiation, such as X-rays, gamma rays, electrons, or protons. The excited atoms emit characteristic secondary X-rays that are indicative of the chemical elements present in the sample and of their relative concentrations. If means are provided for resolving, detecting, and counting the secondary X-rays, a qualitative and quantitative determination of the elements in the sample can be made. Detailed discussions of the theory and practice of XRF spectrometry are available (Refs. 356 through 360).

Two general types of spectrometers for resolving and detecting X-rays are in use: wavelength-dispersive and energy-dispersive spectrometers. Much of the following discussion is taken from Reference 361.

The wavelength-dispersive spectrometer uses a single crystal to diffract X-rays according to Bragg's law:

$$\lambda n = 2d \sin \theta \qquad (4\text{–}51)$$

where

d = the interplanar spacing of the diffracting planes, Å
n = the order of the diffracted beam
λ = wavelength, Å
θ = the angle between the incident X-rays and the diffracting planes (X-ray spectrometers are usually calibrated in terms of 2θ, the angle between the diffracted beam and the undeflected incident beam.)

An X-ray tube, powered by a high-voltage generator (60 kV or higher) furnishes a continuum of exciting X-rays. Some of these will produce secondary (fluorescent) X-rays in the sample; others will be scattered incoherently. Upon diffraction by the single crystal of the spectrometer and detection by a scintillation or proportional counter, the secondary X-rays become the signal of interest; the scattered primary X-rays, also diffracted and detected, become noise. Only X-rays that are more energetic than a critical energy, characteristic of each element, excite the secondary X-rays; the closer those X-rays are to the critical energy, the more efficient they are in producing the fluorescent X-rays. Primary X-rays with energies below the critical energy produce only noise. A single-channel pulse-height analyzer (PHA) filters out much of the noise and discriminates against unwanted orders of diffraction. The combination of a crystal spectrometer with a single-channel PHA constitutes a true monochromator.

In energy-dispersive spectrometry, the source of exciting X-rays may be an X-ray tube, a fluorescing element excited by X-rays, or a radioisotope source (^{109}Cd, ^{57}Co). The exciting X-rays again produce secondary X-rays from the specimen that are detected by a semiconductor detector, usually Li-drifted Si or Ge, or high-purity Ge. The amplitudes of the electric pulses generated in the detector by individual X-ray photons are proportional to the energy of the photons and are sorted accordingly by a multichannel PHA. The spectrum is generated by mathematically unfolding the raw data stored in the PHA with a computer.

Both wavelength-dispersive and energy-dispersive systems have advantages and disadvantages. Both have been used for the determination of U and Pu. Wavelength-dispersive systems offer high resolution, but low efficiencies, so that X-ray tubes are required for excitation. Wavelength-dispersive systems excel at quantitative analysis, because of the comparative freedom from interference by incoherently scattered primary radiation. This is especially important in the analysis of liquids. Signal-to-background ratios are high; most of the detected radiation is useful signal. The high resolution of wavelength-dispersive spectrometers is an asset in the analysis of spent fuel solutions where there is a potential for interference from fission product radiations.

Energy-dispersive systems are more efficient but have poorer resolution at energies below 20 keV. The high efficiency is often an asset in measurements of "cold" solutions when radioisotopic excitation sources are used. Qualitative analysis is more rapid with an energy-dispersive spectrometer. However, energy-dispersive systems have the disadvantage that the detector and PHA must process every photon that strikes the detector. This leads to low signal-to-background ratios, and a lower count-rate tolerance than with wavelength-dispersive spectrometers. In energy-dispersive systems, only about 10% of the total counts represent useful signal.

For U and Pu measurements, X-ray lines in the *K*, *L*, or *M* series may be used. The more intense lines in these series are listed in Table 4.47. Thorium is also included, since it is often added as an internal standard. The main considerations in selecting a line are its intensity above background and freedom from interference from adjacent lines.

Table 4.47 X-ray lines commonly used for uranium and plutonium

	Energy (keV)		
Line	Thorium	Uranium	Plutonium
$K\alpha_1$	93.350	98.440	103.763
$K\beta_1$	105.609	111.303	117.256
$L\alpha_1$	12.969	13.612	14.276
$L\alpha_2$	12.810	13.437	14.082
$L\ell$	11.119	11.616	12.122
$L\beta_1$	16.202	17.217	18.291
$L\beta_2$	15.624	16.428	17.255
$L\gamma_1$	18.902	20.164	21.414
$M\alpha$	2.993	3.167	3.356
$M\beta$	3.146	3.336	3.550

The high energies of the *K* series lines require either the use of generators and X-ray tubes capable of producing up to 150-keV X-rays, or the use of gamma-ray excitation sources. Diffraction gratings or crystals that provide good dispersion in this energy region are not available, so energy-dispersive systems must be used. In addition, there may be significant overlap of Pu gamma rays with the U and Pu X-rays. Nevertheless, *K* series X-rays have been applied to solution analysis (Ref. 362). Use of the *M* series X-rays requires either a helium or vacuum path to minimize air absorption, and use of these lines usually is limited to solids. Because of the close proximity of the Th, U, and Pu lines, wavelength-dispersive systems must be used. Even then, serious problems can result from the overlap of the $M\alpha$ and $M\beta$ lines of Pu by the $M\beta$ and $M\gamma$ lines, respectively, of U and of the $M\alpha$ and $M\beta$ lines of U by the $M\beta$ and $M\gamma$ lines of Th. Nevertheless, *M* series lines have been used for some types of analyses (Ref. 363).

The most common choice is one or more of the *L* lines. They provide good intensities in an air path for analyses of solutions or solids, and can be used with any type of excitation or detection system.

When a wavelength-dispersive spectrometer is used, X-ray lines are commonly quoted in terms of wavelengths in angstroms. With energy-dispersive spectrometers, energies in kiloelectron volts are quoted. The two units are related by

$$E = \frac{12.396}{\lambda} \qquad (4-52)$$

where

E = photon energy, keV
λ = wavelength, Å

Scope of Applications

The first applications of XRF spectrometry were to the analysis of unirradiated materials, such as U and Pu alloys, oxide and carbide fuels, and various types of solutions. In general, methods have covered the concentration range of 0.003 to 10 g U or Pu/L, and a precision of 1% RSD or better was attained at the 1-g/L level. More recently, XRF spectrometry has been applied to the analysis of irradiated fuel solutions. Solutions with initial activities up to 1000 Ci/L prior to dilution for analysis have been handled. Solutions have either been analyzed directly (after dilution, if necessary), or a small volume of the diluted solution was mixed with an internal standard solution and an aliquot of the mixture deposited on filter paper. Precisions and accuracies of 1% or better were attained in most of the procedures.

Summary of Performance

Table 4.48 lists the performance of the X-ray fluorescence methods for the determination of U and Pu in several irradiated and unirradiated materials. A discussion of specific applications is presented later in this section in discussions that correspond to the literature, user, and exchange program source categories in the table.

Equipment

There are two basic types of XRF spectrometers: wavelength-dispersive and energy-dispersive. Diagrams of these two types are shown in Figures 4.18 and 4.19. The wavelength-dispersive instruments will consist of a high-voltage generator (usually 60 to 100 kV, 50 to 60 mA) and X-ray tube, a crystal spectrometer with precision goniometer, a detector and high-voltage power supply (usually 2 to 3 kV), preamplifier, linear amplifier, single-channel pulse-height analyzer, scaler and timer, ratemeter, and stripchart recorder. Automated wavelength-dispersive instruments under computer control are available in versions in which the desired X-ray lines are measured either sequentially or simultaneously.

The energy-dispersive instruments consist of an X-ray tube and generator or power supply; a semiconductor detector and cryostat; preamplifier; linear amplifier; various other modules for peak-shaping, baseline restoration, and dead-time correction; a multichannel pulse-height analyzer; and a computer.

Costs for XRF spectrometers range from $60,000 to $150,000 or more, depending on the extent of automation, the computing capability, and the software supplied. The user should expect to have to develop additional software for his application, at a cost that may match or exceed the instrument costs.

Table 4.48 Summary of performance: uranium and plutonium by XRF

Application	Assay	Method	Performance (% RSD)		Source[a]
			Random Error	Systematic Error	
Product material:					
UO_2 powder	U	WD, Sr internal standard	0.15	—	E
U metal, NBS 960	U	WD, Sr internal standard	0.33[b]	0.085	U
U-carbide	U	WD	0.2	—	L
U-Mo-Ru alloy, 95% U	U	WD, Sr internal standard	0.11[b]	0.034	U
UO_2-Al_2O_3	U	WD	1.8	—	L
UO_2-stainless steel	U	WD, Sr internal standard	0.5 to 1.0	—	L
(Pu,U)O_2 powder	U	WD, Sr internal standard	0.31	—	E
	Pu	WD, Y internal standard	8.5	—	U
	U or Pu	WD, Th internal standard	0.4	—	L
	U or Pu	WD or ED, on-line	0.2,0.5	—	L
(U, Th)C process sample	U	WD, Sr internal standard	0.80[b]	0.085	U
(U, Th)C, SiC coated, working standard	U	WD, Sr internal standard	0.26	1.0	U
(U, Th)C, SiC coated, process sample	U	WD, Sr internal standard	0.61[b]	1.0	U
Solutions:					
UNH	U	WD, Sr internal standard	0.41	—	E
Pu$(NO_3)_4$	Pu	WD, Y internal standard	4.0	—	U
(U, Th) solution	U	WD, Sr internal standard	1	—	L
U solution	U	WD	5	—	L
	U	ED, ^{109}Cd	0.4	—	L
Pu solution	Pu	WD, Y internal standard	1.2	—	L
U or Pu solution	U or Pu	WD, Th internal standard	1	—	L
Low-level U solution, 10 to 200 μg/mL	U	ED, ^{109}Cd	3.7 to 44	0.95 to 11	U
Low-level U waste solutions	U	ED, ^{109}Cd	57[b]	—	U
LWR/fast breeder reactor irradiated solutions	U or Pu	WD, Th or Y internal standard	1(0.5 to 3)	—	L

Note—See footnote at end of table.

Table 4.48 Summary of performance: uranium and plutonium by XRF (Cont'd)

Application	Assay	Method	Performance (% RSD)		Source[a]
			Random Error	Systematic Error	
Irradiated dissolver solutions	U or Pu	ED, Ti external standard	1	—	L
	U or Pu	WD, automated, on-line	0.5 to 1	—	L
Irradiated product solutions	U or Pu	ED	0.3	—	L
Scrap:					
PuO_2, 0.43 g Pu/g	Pu	WD, Y internal standard	2.9	—	U
Pu solids	Pu	WD, Y internal standard	0.63	—	L
Pu muds	Pu	WD, Y internal standard	10	—	L
U-Mo-Ru alloy, 0.2% to 80% U	U	WD, Sr internal standard	0.27 to 84[b]	0.034	U

ED = energy dispersive; WD = wavelength dispersive.

[a] E = survey of exchange programs; L = literature survey; U = users' survey of production facilities.

[b] Includes sampling error.

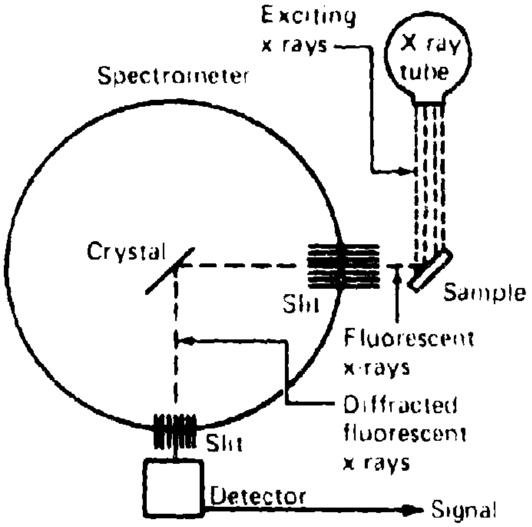

Figure 4.18 Wavelength-dispersive XRF system (from Ref. 361).

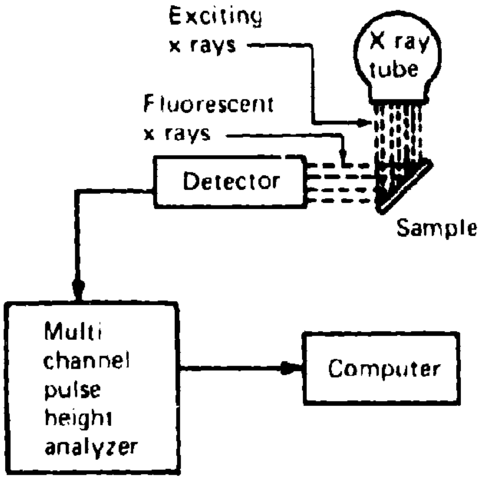

Figure 4.19 Energy-dispersive XRF system (from Ref. 361).

Major Sources of Error

Sources of Error (Ref. 356)

Statistical counting error depends only on the total accumulated count.

Instrumental errors include variations or drift in the X-ray tube potential and current, drift in detector potential, changes in crystal interplanar spacing due to temperature changes, coincidence (dead-time) losses in the detector and electronic circuitry, shift and distortion of pulse-height distributions, and instability or drift in the electronic circuity.

Operational errors consist of nonreproducibility in settings of instrument conditions.

Errors may also be incurred in estimating the concentration from the calibration curve.

Interferences

Three types of matrix interference are encountered in X-ray fluorescence: line overlap, absorption, and enhancement.

Line interference occurs when a matrix element has an emission line that overlaps that of the SNM. In the 11- to 20-keV energy region, the elements from As to Mo have one or more strong K lines that are close enough in energy to the commonly measured L lines of Th, U, and Pu to be a possible source of interference. Unfortunately, many of these elements appear as fission products in spent fuel. Strontium interferes strongly with the measurement of Pu.

Absorption and enhancement are essentially two manifestations of the same phenomenon. Absorption, which occurs in varying degrees in all samples, is the more serious of the two. Both the matrix and SNM can attenuate the SNM line, causing a negative bias in the assay result. Matrix enhancement occurs if a matrix element has a strong X-ray line above the energy of the absorption edge of the SNM analyte. For example, if Mo is present in a U solution, the Mo $K\alpha_1$ line can excite the U $L\alpha$ lines and cause a positive bias in the U measurement. For U and the transuranics, self-enhancement also can occur (Ref. 364). For these elements, the $L\beta_1$ emission line is above the L_{III} absorption edge in energy and can excite the L lines commonly used for measurement. Self-enhancement is generally not noticeable unless large quantities of U and Pu are present.

The internal-standard method corrects for matrix absorption-enhancement effects by adding a known standard to the solution and comparing the counts in the SNM line to the counts in the standard line. The standard line is chosen as close to the analyte line as possible, preferably with an absorption edge above the energy of any enhancing matrix lines. Different internal standards, including Sr for aqueous solutions and bromobenzene for organic solutions, have been used in the measurement of Th and U at different stages of solvent extraction (Ref. 365). It has been pointed out, however, that bromobenzene, due to its volatility, can lead to large errors in the analysis (Ref. 366). Zirconium also has been suggested as an internal standard for organic U and Th solutions (Ref. 367). Thorium is the commonly used internal standard for U and Pu solutions (Refs. 366, 368, 369, and 370), but Y also is used when the possibility of Th contamination exists in the sample, as would be the case for Thorex reprocessing samples.

Measurement Control Requirements

Reference materials or synthetic standards, with accurately known Pu and/or U content must be analyzed daily or during each shift. The use of an internal standard (or if this is not possible, an external standard or flux monitor) helps to correct for changes in instrument conditions or sample matrix. Reference materials should bracket the concentration range of the samples to be analyzed.

Data Analysis Requirements

The calculations required will depend on the application and the procedure used. For an unirradiated U or Pu solution, to which an internal standard has been added, a calibration curve plotting the ratio of intensities (counts) of the U or Pu line to the internal standard line versus the concentration of U or Pu will have been prepared. On subsequent analyses, one may estimate the SNM concentration from the calibration curve, or calculate it by use of an equation that has been fitted to the calibration data.

In the analysis of irradiated solutions, it is generally necessary to obtain the XRF spectrum and the spectrum of the natural radioactivity and calculate the difference spectrum. If peak fitting and unfolding is required, the computer programs can become quite lengthy and complex (Ref. 371). Such programs may also correct for enhancement or absorption.

Survey of Selected Literature

Tables 4.49 and 4.50 list several applications and corresponding performance of the method as applied to several unirradiated and irradiated materials. The analysis of irradiated nuclear fuel dissolver solutions and of process and product solutions encountered in reprocessing operations is a field in which there is much interest. A brief discussion of some recent work in this field follows.

Several systems have been developed to assay highly radioactive spent fuel solutions. One of these systems (Refs. 369 and 370) uses a wavelength-dispersive spectrometer to assay solutions with U-Pu ratios of 50:1 to

Table 4.49 Some applications of XRF spectrometry to unirradiated materials

Type of Sample	Concentration Range	Recovery[a]	Precision (% RSD)	Comments	Ref.
Uranium solutions	>0.05 g/L	—	5(1 g U/L)	WD.	372
Nitric acid or TBP solutions	U: 0.25 to 6 g/L; Th: 0.22 to 266 g/L	99% to 101%	1	Internal standard: Sr (aqueous) or bromobenzene (organic), WD.	365
	0.003 to 10 g/L U or Pu	—	1(1 g/L)	Internal standard: Th; WD.	368
Plutonium in liquids, solids, or Pu-poor muds	Liquids: 5 to 250 g/L Solids: 10 μg/g to 100%	—	Liquids: 1.24 Solids: 0.63 Muds: 10 (10 to 1800 μg/g)	Internal standard: Y; WD.	373
Nitric acid or TBP solutions	0.5 to 100 g U/L	—	0.4 (5 to 25 g/L)	^{109}Cd source; source transmission also measured; ED.	374
UO_2-Al_2O_3 fuel	Approximately 1 g U/L	99%	1.8	Sample fused with potassium pyrosulfate; melt dissolved in water + H_2SO_4. WD.	375
Uranium carbides		—	0.2	Sample fused with borax and BaO_2; melt poured to form pellet; WD.	
UO_2-stainless steel	15% to 25% UO_2	99.5%	0.5 to 1.0	Internal standard: Sr; sample dissolved in aqua regia, then fumed with perchloric acid; WD.	377
Plutonium-uranium fuels (mixed oxides), Haynes alloy mixtures with Pu, Ta-Pu.	0.5% to 25% PuO_2, 75% to 99.5% UO	—	0.4	Sample fused with potassium pyrosulfate; melt poured to form pellet; internal standard: Th; WD.	364
MOX fast breeder reactor fuels	20% to 30% PuO_2	—	0.5	Pellets analyzed; on-line analysis in fuel fabrication plant possible; WD.	378
	25% PuO_2	—	0.2	Pellets to be analyzed on-line; automated system under development; ED.	379

ED = energy dispersive; WD = wavelength dispersive; TBP = tributylphosphate

[a] Recovery = (quantity found/quantity taken) × 100.

Table 4.50 Some applications of XRF spectrometry to solutions of irradiated fuels

Type of Sample	Concentration Range	Radiation Levels	Recovery or Accuracy (%)	Precision (% RSD)	Comments	Ref.
Fast breeder reactor fuels, after partition	Pu: 1 to 20 g/L	1Ci/L[a]	1[b]	1	Internal standard: Y; WD.	380
LWR dissolver solution	U: 0.05 to 18 mg/g Pu: 0.6 to 1.2 mg/g	1.3 Ci/g	U: 97.8 to 105.2[c] Pu: 98 to 102[c]	1 to 3	Internal standard: Th; WD; sample analyzed as solution.	369
Fast breeder reactor fuels, dissolver solution or organic extract (1*M* nitric acid or 20% TBP-80% dodecane).	1 to 200 g U,Pu/L	<1000 Ci/L	—	1 (>10g/L)	Internal standard: Th; Solution deposited on filter paper[d]; WD.	368
LWR dissolver and product solutions:						
Dissolver	U: 14 to 220 mg/g Pu: 0.5 to 1.5 mg/g	<1000 Ci/L	0.58[b] 0.95[b]	0.45 —	Internal standard: Th; WD.	370
Product	U: 280 mg/g Pu: 1.6 to 46 mg/g		0.3[b] 0.53[b]	0.75 0.45		
Dissolver solution	U: 50 g/L Pu: 0.12 to 0.62 g/L	2 Ci/g	2[b]	1	Ti external standard: ED; sample deposited on polycarbonate substrate.	381
LWR fuels	U: 20 to 40 g/L Pu: 0.2 to 0.4 g/L	1000 Ci/L		1	WD.	382
Product solution	Pu,U: 0.001 to 4g/L	100 Ci/L		0.3	ED: pyrographite scattering chamber; Se monitor.	383
	Pu,U: 1 to 200 g/L	2.8 m Ci/g Pu	0.3[b]	—	^{57}Co sources excite *K* X-rays of U and Pu; ED: spectrum unfolding required to separate Pu $K\alpha_2$ from U $K\alpha_1$.	371

Note—See footnote at end of table.

Table 4.50 Some applications of XRF spectrometry to solutions of irradiated fuels(Cont'd)

Type of Sample	Concentration Range	Radiation Levels	Recovery or Accuracy (%)	Precision (% RSD)	Comments	Ref.
LWR dissolver solution	U: 300 g/L Pu: 3 g/L	1000 Ci/L	—	0.5 to 1	Monochromator plus WD spectrometer: sample circulates from tank through sample cell; On-line automated system under development.	361, 384

ED = energy dispersive; WD = wavelength dispersive; TBP = tributylphosphate

[a] Maximum activity of analytical sample: 10 mCi/L.

[b] Accuracy.

[c] Recovery = (quantity found/quantity taken) × 100.

[d] Maximum activity on filter paper: 10 mCi.

300:1. Accuracies and precisions of better than 1% have been obtained with analysis times of 2 to 5 min. Solutions having activities up to 1000 Ci/L are handled routinely by making a 200-µL aliquot, mixing it with 100 µL of a Th standard solution, and depositing 20 µL of the mixture (containing 0.01 to 2 mg of U or Pu) on filter paper (Ref. 366). The maximum activity on the filter paper is 10 mCi, and there is no interference from radioactivity with the XRF measurement. If the initial sample solution has >10 mg U or Pu/mL, the reproducibility of the measurement is within 1%. Samples having low beta-gamma-ray activities can be analyzed directly in solution after addition of an internal standard. The fission products cause no serious line interference. An automatic sample-preparation system is being developed to allow on-line analysis (Ref. 370).

Uranium and Pu in solution having beta-gamma activities to 1 Ci/L have been measured directly through a Plexiglas window (Ref. 380). The system used is as close to in-line analysis as one can devise. An automatic sampler removes solutions from the sample line and yttrium is added to serve as an internal standard. Solution transfers are made by pneumatic tube. A minicomputer performs data reduction, and overall precision and accuracy of better than 1% are claimed for the technique.

In another system (Refs. 381 and 385), hot dissolver solutions containing U and Pu at ratios up to 400:1 and U concentrations of ≈50 g/L are measured with a low-powered X-ray tube in combination with a Si(Li) detector. Preliminary tests indicate that accuracies of 2% and a precision of 1% RSD are possible with 10-min analysis times. Preparation of samples by freeze-drying has been evaluated (Ref. 386), and the preparation of standards has been investigated (Ref. 387).

A proposed wavelength-dispersive system (Refs. 361 and 388) should be able to measure high concentrations of U and Pu in irradiated samples to a precision of 0.2% RSD. The system consists of a highpower rotating-target X-ray tube; monochromator, for providing monochromatic exciting radiation; sample cell connected in a recirculating loop to the solution tank; X-ray spectrometer; and computer for controlling the data-taking process and performing calculations. The total sampling concept has been demonstrated (Ref. 384).

A system has also been developed for automatic sampling and sample preparation of dissolver solutions from the reprocessing of Th-U fuels (Ref. 367). For solutions with activities up to 2000 Ci/L, samples containing 1.0 mL of solution are automatically aliquoted and mixed with an internal standard. The aliquots are evaporated onto a filter paper, which is transferred to a shielded X-ray spectrograph. All operations are performed remotely under computer control. By analyzing the samples as thin films, the scattered background is reduced compared to the sample signal, thus increasing sensitivity and reducing counting times. Measurements of thin films are linear with the concentration of nuclear material over a small range, above which saturation effects become important.

Two energy-dispersive systems have been devised for the analysis of product solutions. One system (Ref. 383) employs a scattering chamber containing 24 pyrolytic graphite crystals in a tungsten block to reduce scattered exciting radiation and gamma radiation from the sample. A low-powered transmission X-ray tube with demountable Ag and Mo anodes provides the exciting radiation. The intensity of the beam is monitored with a Se disk. The U and Pu $L\alpha$ X-rays and the Se $K\alpha$ and $K\beta$ lines are measured with a Si(Li) detector. A precision of 0.3% RSD is claimed. Solutions may have a fission product activity up to 100 Ci/L. The other system uses two ^{57}Co sources to excite the K X-rays of U and Pu, which are detected by a high-purity Ge detector (Refs. 362 and 371). The sample must be analyzed without the sources to record the radioactivity spectrum. This must be subtracted from the total (XRF plus radioactivity) spectrum to get the net XRF spectrum. A computer-based analyzer system collects the spectra, fits and unfolds peaks, corrects for enhancement and absorption and obtains concentrations from the calibration equations. Minor fission product contamination (up to 2.8 mCi/g Pu) is permissible. The lines measured are U $K\alpha_1$ plus Pu $K\alpha_2$ and Pu $K\alpha_1$. One must then unfold Pu $K\alpha_2$ to get the U $K\alpha_1$ value. Alternately the U $K\alpha_2$, which has no interference but lower signal-to-noise ratio, can be measured. A change in U/Pu ratio requires correction of the calibration equation.

All of these methods require calibration with synthetic standards. The U and Pu concentrations, the U/Pu ratio, and the acidity of the solution must be as similar to the samples to be analyzed as possible.

Survey of Production Facilities

Three X-ray fluorescence procedures for determining U and one for determining Pu have been described by user facilities.

The first method for U is applied to low-level waste solutions. An energy-dispersive system using a ^{109}Cd gamma-ray source is used and the $L\alpha_1$ 13.613-keV X-ray is detected and analyzed with a Si(Li) detector/single-channel pulse-height analyzer to give U concentration directly in micrograms per milliliter. Random errors of 3.7% to 44% RSD have been obtained for the repetitive measurement of standard solutions of 10 to 200 μg U/mL. Waste solutions (NO_3^-, F^-) yield a random error of 57% RSD including sampling uncertainty. The systematic error of the method based on the random error of the mean of the calibration verification standard determinations ranges from 0.95% to 11% RSD.

The other two applications for determining U employ a wavelength-dispersive spectrograph. A Sr internal standard is added to the sample and the Sr $K\alpha$ and U $L\alpha$ peaks are detected with a LiF crystal. Results are obtained from a calibration curve of U concentration versus the U/Sr count ratio. The method has been applied to U-Mo-Ru alloy product (95% U) and scrap materials. The method has also been applied to HTGR (U,Th) carbide materials. The random and systematic errors for the method are given in Table 4.51.

Table 4.51 Performance of wave length dispersive XRF methods at production facilities

Application	Random Error (% RSD)	Systematic Error (% RSD)
U-Mo-Ru alloy, 95% U	0.11[a] (0.058-0.17)	0.034
U-Mo-Ru dross, 80.5% U	0.49[a]	0.034
U-Mo-Ru fines, 78% U	0.27[a]	0.034
U-Mo-Ru glass, 3.6% U	31[a]	0.034
U-Mo-Ru contaminated glass, 0.37% U	52[a]	0.034
U-Mo-Ru clean glass, 0.23% U	84[a]	0.034
(U, Th)C process sample	0.80[a]	0.085
(U, Th)C, SiC-coated, working standard	0.26	1.0
(U, Th)C, SiC-coated, process sample	0.61[a]	1.0

[a] Includes sampling error.

A method employing a Y internal standard and wavelength-dispersive spectrograph has been applied to the determination of Pu in solutions. The Y *Kα* and Pu *Lα* X-rays are detected with a LiF scintillator. The Pu concentration is then determined from a calibration curve of Pu concentration versus the Pu/Y count ratio. The random errors of the method as applied to solutions of the various materials are as follows:

Material	% RSD
$Pu(NO_3)_4$, 32 g/L	2.5
$Pu(NO_3)_4$, 79 g/L	5.4
PuO_2 scrap, 0.43 g/g	2.9
$(Pu,U)O_2$ powder, 0.33 g/g	8.5

Survey of Exchange Programs

SALE program (Ref. 154) participants use X-ray fluorescence for determining U in UO_2 powder, MOX, and UNH solution. The method described employs a Sr internal standard and measurement of the U *Lα* and Sr *Kα* X-rays. Uranium concentration is obtained from a calibration curve of the U/Sr count ratio versus U concentration. It is assumed that wavelength-dispersive spectrometry is employed. The random errors of the method as applied to the above materials are as follows:

Material	% RSD
PuO_2 powder	0.15
$(Pu,U)O_2$ powder	0.31
Uranyl nitrate (UNH)	0.23, 0.59

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Open literature items, such as books, journal articles, and professional society publications, are available in public and technical libraries. Reports published by or for the U.S. Nuclear Regulatory Commission (NRC) are available for purchase from the NRC/GPO Sales Program, Washington, DC 20555, and from the National Technical Information Service, Springfield, VA 22161. These publications are also available for inspection and copying for a fee at the NRC Public Document Room, 1717 H Street, N.W., Washington, DC. Foreign reports listed are available from the originating organization. Reports prepared by the National Laboratories, the former U.S. Atomic Energy Commission, and the Department of Energy, as well as those of other Government agencies, are available from the National Technical Information Service, Springfield, VA 22161. ANSI publications are available from the American National Standards Institute, 1430 Broadway, New York, NY 10018, Copyrighted.

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CHAPTER 5

Passive Nondestructive Assay Methods

5.1 INTRODUCTION

Passive nondestructive assay (NDA) methods are based on the detection of radiation emitted by the material itself without external stimulation. Gamma rays, X-rays, neutrons, alpha particles, and heat generation from radioactive decay are signals used for passive assay. Three applications of passive assay are discussed in this chapter. These are determinations of (1) U and Pu content, (2) U and Pu isotopic composition, and (3) holdup. Several techniques to be described can be used for more than one application. This chapter deals with a number of very different techniques, all (except densitometry) based on the consequences of alpha and beta particle decay or spontaneous fission of the special nuclear material (SNM). SNM is defined as Pu or U enriched in ^{233}U or ^{235}U. Methods of determining total SNM content through measurement of the magnitude of the passive signal are discussed in Section 5.2. Isotopic composition determinations may be made by measuring gamma rays for a particular isotope or from groups of isotopes of a particular element. These techniques are discussed in Section 5.3. Holdup measurements (the assay of the amount of SNM contained in process equipment), discussed in Section 5.4, may be used to complete a total plant inventory.

5.1.1 Scope of Chapter

The techniques treated in this chapter are "passive" rather than "active" in that no external source is used to stimulate a response from the material. For example, an active system for the analysis of U might use a neutron source to induce fissions and would detect the coincident fission neutrons. A passive system for Pu would not use a neutron source but would detect the coincidence neutrons occurring from spontaneous fission. This chapter also includes those assay techniques based on gamma-ray attenuation, gamma-ray absorptiometry, and *K*- and *L*-edge densitometry. (See Sections 5.2.1.4 through 5.2.1.6.) These techniques are not "passive" because the signal is not from the spontaneous decay of the material; however, it seems appropriate to include them with the gamma spectrometry discussion of Section 5.2. Active NDA methods are described in Chapter 6.

5.1.2 Uses of NDA

NDA can be used to assay closed containers of SNM-bearing materials in a relatively convenient and timely fashion. Passive NDA techniques have been developed for scrap and waste measurements in which analytical techniques are inadequate because, as the result of the heterogeneity of the material, it is difficult to obtain a representative sample. Passive assay of pure, homogeneous material is also used in some applications because it is less expensive and more timely. Assay times can range from a fraction of a minute to hours depending on the NDA technique and properties of the measured item. The short assay times can allow for measurement of every item in a process stream in certain cases.

Both passive and active NDA can yield timely and accurate results. Passive assay systems are found to be simpler than active ones because the latter require neutrons or high-energy gamma rays from either a radioactive source or an accelerator target. The advantage of an active system, however, is that passive radiation that could be used for assay may not be emitted in sufficient intensity to be useful. Moreover, in certain applications spontaneous radiation may be emitted in sufficient intensity but have such low penetrability that measured intensity could not be related to SNM content. In these cases active assay would be the preferable NDA technique.

5.1.3 Calibration of Passive NDA Systems

A fraction of the passive radiation emitted by the SNM is absorbed or scattered by other material. An attenuated fraction of the total radiation reaches the detector where another fraction is converted into electronic signals that are finally counted for a fixed period. Rather than calculating each attenuating effect explicitly, which may not be feasible in many cases, physical standards that closely match the materials to be measured are prepared "in-house" and are used for calibration of the NDA system. Instrument response per gram of SNM is then determined. The SNM content and isotopic composition of the physical standards are established through chemical techniques, including mass spectrometry. These chemical methods themselves are calibrated through reference materials with assigned values established by the National Bureau of Standards (NBS), International Atomic Energy Agency (IAEA), or the New Brunswick Laboratory (NBL).

Each significant change in matrix or isotopic composition can cause different attenuating effects, and, as a result, a different set of physical standards is needed for each category of material to be measured (for example, "combustible waste" versus "hard scrap"). The standards must be packaged in the same kind of container as the unknowns and counted in an identical configuration. Within some facilities many sets of standards may be necessary to cover all material categories because of the variety of matrix forms and chemical compositions in which SNM occurs. The NBL and NBS fabricate and certify certain NDA physical standards.

For each material category, only one physical standard may be necessary for calibration if its material properties and SNM content are nearly identical to the unknown. If considerable variability in SNM content of the unknowns is to be expected and if the quantity of SNM is appreciable, a number of calibration standards will be needed. A calibration line will need to be fitted to the data to determine instrument response for varying SNM content. ANSI standard N15.20–1975 (Ref. 1) recommends that at least $P + 1$ calibration standards with distinct masses be used, where P is the number of parameters in the fitted equation.

The purpose of using this many standards is to acquire enough independent data to statistically evaluate whether the calibration curve correctly represents the data and to provide an estimate of the calibration or systematic error that results from using the fitted curve.

Recalibration of the NDA system may be required if the original standard set is no longer representative of the items being measured or if significant changes are made in instrument hardware or settings. Certain NDA systems are known to be sensitive to environmental changes. For example, the instruments using photomultipliers (PMs) for detecting the light from scintillators are sensitive to temperature changes and to changes in PM voltage. These instruments should be checked several times daily using check sources. Corrections may be needed to compensate every assay value for instrument drift with unstable systems.

Clear operating procedures are required for personnel who run NDA systems. These can be simplified in automated systems interfaced to small computers and may require only simple responses to computer-generated questions. All systems are used most effectively by people with some background in electronics, because system setup and testing generally require some familiarity with electronic test equipment, especially oscilloscopes. There should be an awareness of criticality and radiological safety in sample handling.

In this chapter several sections are concerned with the function of the detectors used for the various assay methods. An excellent textbook and reference for more detailed information is *Radiation Detection and Measurement* by G. F. Knoll (Ref. 2).

5.2 DETERMINING TOTAL SNM

The U and Pu content of a wide variety of samples can be assayed by passive NDA methods. These methods depend on the signal from a particular isotope of the element, for example, the 186-keV gamma ray from ^{235}U. The intensity of the signal can be used to determine the isotopic content of the sample. Additional isotopic information is required to transform the measured quantity into grams of U or Pu. This requirement arises because passive techniques are related to the nuclear properties of a particular isotope or isotopes but not to the elemental (chemical) properties of the SNM. Passive assay methods for isotopic composition determinations are given in Section 5.3. The other principal method used is mass spectrometry, which is described in Chapter 4.

The passive techniques for determining SNM content rely on unique gamma-ray, X-ray, neutron, or alpha particle emission properties. For gamma rays and X-rays, spectral analysis systems are used to separate the gamma ray or X-ray of interest from interfering radiations. These systems are discussed in Section 5.2.1.

For neutrons, because detailed spectral analysis is not practical, neutron counting without energy analysis is used for assay. Both U- and Pu-bearing materials emit neutrons in sufficient intensity to be useful for assay purposes. These can result from spontaneous fission or from (α,n) reactions on matrix material elements with low atomic numbers (low Z) such as oxygen or fluorine. This latter source of neutrons can complicate the interpretation of results from counting of single neutrons. (See Section 5.2.2.) This complication is minimized in the neutron and neutron plus gamma-ray coincidence systems discussed in Section 5.2.3.

Alpha particles from the decay of SNM may be counted directly (Section 5.2.4) or indirectly by calorimetry (Section 5.2.5) through the heat generated by the transformation of their kinetic energy to heat in the assay material. Calorimetry is a well-developed methodology and is used for Pu assay. The interpretation of heat generation, however, is dependent upon knowledge of the Pu isotopic composition. Passive gamma-ray measurements can be used for isotopic composition determinations as an adjunct to calorimetry.

5.2.1 Passive Gamma-Ray and X-Ray Spectroscopy

Useful gamma-ray signatures occur for nearly every isotope of U and Pu currently handled in appreciable quantities. The major gamma rays from U and Pu decay are listed in Table 5.1 (from Ref. 3). Uranium or Pu content is usually determined by the 185.72-keV gamma ray of ^{235}U or the 413.69-keV gamma ray of ^{239}Pu. Although the intensity of gamma rays from ^{238}U daughters is several orders of magnitude below all other isotopes listed in this table, these gamma rays have also been used to measure U content. Of the isotopes listed, only ^{242}Pu does not emit gamma rays in sufficient intensity to be useful; ^{240}Pu has weak lines that can be analyzed by using computerized peak fitting routines to fit spectra measured by Ge detectors. The 60-keV gamma ray from ^{241}Am decay is also included because ^{241}Am is present in most Pu samples as the result of the beta decay of ^{241}Pu.

Table 5.1 Major gamma-ray signatures for the fissionable isotopes^a

Isotope	Energy (keV)	Intensity $(g \cdot s)^{-1}$	Comments
^{235}U	185.72	4.3×10^4	The only intense gamma ray. Resolved with NaI as well as Ge(Li). Useful for enrichment and quantitative measurements. Several much weaker peaks are seldom useful.
^{238}U	1001.10	1.0×10^2	These actually arise from the ^{234m}Pa daughter of ^{238}U. After chemical separation, about 100 days are required for the activity to come into equilibrium at the levels stated. Plutonium-238 gives rise to the same 766.40-keV gamma ray and would produce interference in U/Pu mixtures. Useful for work with Ge(Li) or NaI.
	766.40	3.9×10^1	
^{238}Pu	766.40	1.5×10^5	Most useful for quantitative assay with Ge(Li) or NaI. Useful for isotopic determination with Ge(Li).
	152.77	6.5×10^6	
^{239}Pu	413.69	3.4×10^4	The 413.69-keV gamma ray usually provides the basis for Ge(Li) assays. The 413.69-keV gamma ray plus the 375.02-keV gamma ray and its weak neighbors form a complex upon which NaI assays are based (385-keV complex).
	129.28	1.4×10^5	Useful for isotopic determinations with Ge(Li). Plutonium-239 has over 100 gamma rays, some of which are useful for careful work with Ge(Li).
^{240}Pu	—	—	Several weak gamma rays but all suffer bad interference from gamma rays of other isotopes. Requires very careful work with high-resolution detector to make use of any of them.
^{241}Pu	207.98	2.0×10^7	Actually from ^{237}U daughter and requires about 25 days after chemical separation to come into equilibrium at stated value. May also have a few percent interference from ^{241}Am, which emits the same gamma radiation; nevertheless, a good clean strong gamma ray useful with both NaI and Ge(Li).

Note—See footnote at end of table.

Table 5.1 Major gamma-ray signatures for the fissionable isotopes[a] (Cont'd)

Isotope	Energy (keV)	Intensity $(g \cdot s)^{-1}$	Comments
	164.59	1.8×10^{6}	Useful with Ge(Li). Also from ^{237}U.
	148.60	7.5×10^{6}	Useful with Ge(Li). Direct from ^{241}Pu.
^{241}Am	59.54	4.6×10^{10}	Very strong gamma ray but with attenuation problems. Useful with Ge(Li) or NaI. Several other much less intense gamma rays are sometimes useful for Ge(Li) work.
^{242}Pu	—	—	No useful gamma rays at all. *Nature failed us at this point.*

[a] From Ref 3, p. 4. A more detailed list of gamma rays may be found in Section 5.3.1.2 of this handbook.

All the passive gamma-ray and X-ray methods to be discussed use pulse height analysis of the detected radiation. The general principles of the detection and description of the instrumentation are discussed in Section 5.2.1.1. Standards-compensated assay and transmission-corrected assay are of great utility for scrap and waste measurements in which analytical chemical techniques fail because of sample inhomogeneity. In standards-compensated assay (Section 5.2.1.2), attenuation of the SNM radiation can be compensated for by measuring the radiation from a physical standard that duplicates the unknowns in attenuation characteristics. A calibration factor relating SNM content and radiation intensity is thereby obtained that can be applied to the assay of unknown containers. In transmission-corrected assay (Section 5.2.1.3), an additional transmission measurement of an external gamma ray through the unknown is made to correct for variations in matrix attenuation properties.

Absorptiometric methods in which external gamma radiation is used to obtain SNM content through a measurement of the attenuation of gamma-ray intensity at one gamma-ray energy (Section 5.2.1.4) or at several energies (Sections 5.2.1.5 and 5.2.1.6), are discussed. In some applications the thickness of the object to be assayed is much greater than the mean free path of the radiation used for assay. Under certain conditions this circumstance can be used to give a measure of the SNM concentration (Section 5.2.1.7).

Some Pu and U isotopes do not emit radiation in sufficient intensity to be useful for assay purposes. The decay products of certain of those isotopes, however, decay in turn and emit radiation that can be used for assay purposes. The use of this associated radioactivity is discussed in Section 5.2.1.8. Very low concentrations of SNM may be measured using a passive X-ray technique (Section 5.2.1.9). Plutonium/uranium ratios in irradiated reactor fuel may be determined using gamma radiation from fission products having a well-defined relationship to these ratios (Section 5.2.1.10). Application of gamma-ray techniques to isotopic composition and holdup determinations may be found in Sections 5.3.1 and 5.4.1, respectively.

5.2.1.1 Gamma-Ray Detectors and Instrumentation

Gamma-ray detectors use the formation of ions in the detector material by the interaction of gamma rays with atomic electrons (photoelectric effect and Compton scattering) and the atomic nucleus (pair production). Two types of detector materials are generally used for assays: semiconductors and scintillators. The most common type of semiconductor detector is constructed from high-purity germanium (hpGe) or lithium-compensated germanium [Ge(Li)]. Thallium-activated sodium iodide [NaI(Tl)] is the most common type of scintillator. These detector types differ in the manner in which energy deposited by the gamma ray in the detector material is transformed into an electronic pulse. Although subsequent discussion will deal with these two predominant materials, it should be noted that other detector materials are being evaluated. Semiconductor detectors made of CdTe are now being applied to passive assay methods but are currently limited in size. Other types of detector materials, such as HgI_2, are under development and may find safeguards applications.

Semiconductor detectors operate like solid-state ionization chambers. Free charge carriers formed by the gamma-ray interactions are collected from the semiconductor by an applied electric field producing an electrical pulse. The number of electrical charges in the pulse is linearly proportional to the amount of energy deposited in the detector, with about 3 eV required to produce an ion pair for Ge. The pulse is shaped and amplified for use with one or several single-channel analyzers or a multichannel analyzer. These pulse-height analyzers allow one to count the number of pulses with specific amplitudes falling within a range set by the analyst (single channel analyzers) or simultaneously count pulses in many contiguous channels (multichannel analyzers).

A large fraction of the gamma rays striking the detectors is completely absorbed in the sensitive region, giving rise to full-energy peaks in the pulse spectra. The width of these peaks defines the detector resolution and is a measure of the ability to separate the gamma peak of interest from other interfering radiations. The resolution obtained with these detectors depends in part on the size of the detector, with the large detectors often having slightly poorer resolution and slower charge collection times. The latter can limit the tolerable maximum count rate. The energy resolution of Ge detectors is typically 1.8 to 1.9 keV full width at one-half maximum (FWHM) at 1332 keV (^{60}Co). The resolution at 122 keV (^{57}Co) may also be given by the manufacturer and typically ranges from 500 to 1000 eV FWHM. The better resolution (500 eV) is required for isotopic distribution measurements of Pu based on the 100-keV region because of its complicated spectra. The efficiency of Ge detectors is usually given relative to that obtained for a 3-in. diameter, 3-in. thick NaI scintillator for the 1332-keV full-energy peak from ^{60}Co with both detectors 25 cm from the source. Efficiencies of Ge detectors range from <1% to 35%. Higher efficiency detectors allow shorter assay times, but a 25% efficient detector may cost twice as much as a 10% efficient detector, about $18,000 compared to $9000. More details on Ge detectors may be found in Reference 4.

The advantage of the Ge detector over NaI(Tl) is its excellent resolution. [See Fig. 5.1 for a comparison of multichannel spectra obtained with NaI(Tl) and Ge detectors.] Such detectors are especially useful for Pu measurements. The disadvantages are the necessity of cooling the detector to liquid nitrogen temperatures for operation, the higher cost, and the

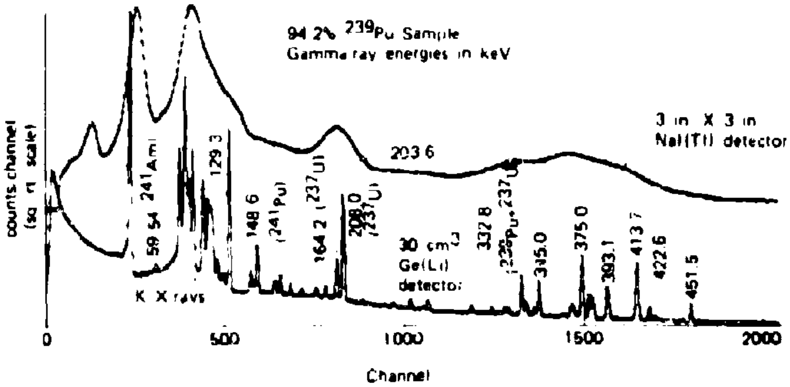

Figure 5.1 Comparison of gamma-ray spectra from NaI and Ge detectors. (Figure courtesy of Los Alamos National Laboratory.)

relatively low efficiency compared to NaI(Tl). Ge(Li) detectors must be cooled at all times while hpGe detectors need to be cooled only while in operation.

Scintillation detectors also generate a signal linearly dependent on the amount of energy deposited. The signal is a light pulse generated by electrons produced by the gamma rays that excite the scintillating phosphor. The scintillator deexcites by emitting light that causes electrons to be emitted from a photocathode. This signal is amplified by a PM, and the output is then shaped and further amplified for analysis. NaI(Tl) is the most common scintillator used. It can be fabricated into various sizes (ranging from 2 cm in diameter and a few millimeters in thickness to greater than 12.7 cm in diameter and thickness). It is hygroscopic and is usually sealed in an aluminum can with a glass window at one end.

The resolution is poorer for NaI(Tl) detectors than for Ge detectors because the light generation mechanism for the scintillator is less efficient in converting the absorbed energy into a useful signal and because the number of photoelectrons emitted by the photocathode will fluctuate significantly for a given absorbed energy. The resolution is at best about 80 keV FWHM at 1332 keV (6%) and about 15 keV FWHM at 122 keV (12%). Thus, this type of detector is used where resolution requirements are not stringent. The main advantages of this type of detector are the high efficiency in detecting a gamma ray, because of the relatively large sizes available and the ease of use. The large sizes can be used for those samples, such as waste material, that contain little SNM and could, therefore, yield an unacceptably low counting rate for less efficient detectors.

Because of the differences in resolution of the NaI and Ge detector systems, the electronics used with each differ also. The Ge systems require an analog-to-digital (A/D) converter coupled with a 1024- to 4096-channel pulse-height analyzer or small computer. Additional electronic components such as a base-line restorer and a pileup rejector are often used to retain the Ge detector resolution in high-count-rate applications. Digital gain stabilization may also be used. The NaI system can be used with an A/D converter and one or two single-channel analyzers or a 128- to 512-channel multichannel analyzer. Both detector systems require stable high voltages. Because of the cooling requirement, the Ge detector systems are bulkier than the NaI systems. Portable hand-held or cart-mounted systems are, however, available for both detector types.

Each system type is sensitive to certain changes in environmental conditions. Scintillator output and PM gain are sensitive to temperature changes. For some crystals these changes are compensated for by using implanted radioactive sources to provide an isolated spectral line for gain stabilization. High humidity can lead to condensation problems in Ge preamplifier systems. Inadvertent exposure of a Ge(Li) detector to fast neutrons will lead to degradation of resolution (neutron fluence greater than or equal to 10^{10} fast neutrons/cm^2). Both types of detectors should be shielded from background radiation. Background count rates of several hundred counts per second are not unusual for an unshielded NaI system. Electronic systems should be protected against voltage surges that might occur during power outages.

5.2.1.2 Standards-Compensated Gamma-Ray Assay

Description of Method

The gamma-ray assay method discussed in this section consists of a simple experimental configuration: a sample holder and a detector with associated electronics. The net number of counts in a gamma-ray peak is determined and is related to the amount of SNM present through calibration standards. The effect of matrix attenuation is dealt with by preparing standards that have nearly identical attenuation properties as the solids or solutions to be assayed. Thus, the calibration of the system relating the counts in a gamma-ray peak to grams of SNM automatically includes the matrix attenuation correction. For all materials, near homogeneity of SNM distribution is assumed. Historically this was one of the first NDA methods used for SNM assay and is still one of the most commonly used techniques. As other gamma-ray passive assay methods have been developed, especially the transmission-corrected assays discussed in section 5.2.1.3, the simple systems described here have been supplanted, at least in part.

Scope of Applications

This form of passive gamma-ray assay is the most common NDA method and has been used in a variety of applications for accountability, process monitoring, quality control, and environmental applications. It has been used to assay the SNM content of solids in containers ranging from small test tubes to 55-gal. (208-L) barrels and 4- by 4- by 8-ft wooden boxes and with SNM quantities ranging from 5 mg to several hundred grams. Samples of solutions contained in vials, test tubes, or sample cells with SNM concentrations ranging from 0.001 to 400 mg/mL are routinely measured. The complete measurement of the entire output of fuel plates or fuel rods from production facilities is another important application of this technique. Online monitoring of process solutions has also been used.

Summary of Performance

Table 5.2 summarizes the performance of several standards-compensated passive gamma-ray systems that are used for accountability measurements by facilities or are reported in the literature. The systems listed use the 186-keV gamma ray for ^{235}U assay and Pu gamma rays in the 400-keV region for Pu assay. The table is divided into three major categories: waste/scrap, small sample, and fuel element. Within each category the table is further divided into types of SNM: highly enriched U (HEU), low enriched U (LEU), and Pu. The performance for each unique matrix/container group, requiring its own specially prepared set of standards, is summarized. The random error of each system is calculated either through the duplicate measurement of production samples or through the replicate measurement of calibration standards over a short (less than several days) time period. The random error is quoted along with average amount of SNM with which this random error should be associated. The systematic error quoted is the systematic uncertainty attached to a measurement that results from the uncertainty in the fitted calibration line. The source column defines whether the results were derived from user accountability and calibration data or literature values given in reports or journal articles.

Equipment

The components for a typical passive gamma-ray system consist of detector, photomultiplier (for NaI), preamplifier, amplifier, timer-scaler(s), and one or more single-channel analyzers (SCAs) or A/D converters with a multichannel analyzer (MCA). For NaI-based systems, a multichannel analyzer is very helpful in setting up the instruments and monitoring pulse height spectra. To fully use the high-resolution capabilities of a Ge detector, a multichannel analyzer with at least 1000

Table 5.2 Summary of performance: standards compensated gamma-ray assay

Material	Matrix and Container	System	Calibrated Range (g SNM)	Assay Time (min)	Performance (% RSD) Random Error	Performance (% RSD) Systematic Error	Source[a]	Ref.
Waste/Scrap:								
HEU >90% ^{235}U	Combustible (compacted) 55-gal. drum	NaI, 2 by 2 in. scan	0 to 15	1	21% at 2.5 g	4.4%	U	—
	Combustible; 55-gal. drum	NaI, 3 by 3 in. scan	5 to 100	5	0.6% at 5 g 0.4% at 100 g	— —	U	—
	Combustible; plastic bag	NaI, 3 by 3 in. scan	0 to 200	1	3.4%	—	U	—
	Combustible; 3- by 7-in cardboard cylinder	NaI, 2 by ½ in. scan	0.1 to 38.0	2	3.5% at 1 g	12% at 5 g 17% at 20.2 g	U —	— —
	Ash; 5-gal. pail	NaI, 3 by 3 in. scan	0 to 25	1.7	7.5% at 7.8 g	3.2% at 1.0 g 3.8% at 12 g	U	—
	Combustible and noncombustible; 55- gal. drum	NaI, 3 by 3 in. scan	2 to 107	10	2.8% at 30 g	10 to 13%	U	—
	Combustible and noncombustibles; 4- by 4- by 8-ft wooden box	NaI, 2 by ½ in. scan	—	2	19% at 12 g	—	U	—
	Noncombustible; 3- by 7-in. cardboard box	NaI, 2 by ½ in. scan	—	2	3.5% at 1.2 g 1.1% at 12 g	9.4% at 5 g 12% at 20 g	U	—
	Machine chips	NaI, 3 by 3 in. scan	5 to 75	1.7	—	20% at 5 g 7.9% at 75 g	—	—

Note—See footnote at end of table.

Table 5.2 Summary of performance: standards compensated gamma-ray assay (Cont'd)

Material	Matrix and Container	System	Calibrated Range (g SNM)	Assay Time (min)	Performance (% RSD) Random Error	Systematic Error	Source[a]	Ref
	Steel jackets	NaI, 3 by 3 in. scan	0 to 10	1.7	—	19%, 1 to 10 g	U	—
	Hard scrap	NaI, 3 by 3 in. scan	18 to 251	1.7	—	14% at 18 g 11% at 250 g	U	—
	Solution (UNH); 55-gal. drum	NaI, 3 by 3 in. scan	2 to 100	5	0.6% at 40 g	0.7%	U	—
	Grinder grit; 5 gal. pail	NaI, 3 by 3 in. scan	0 to 50	1.7	4.3% at 2 g 1.0% at 50.0 g	0.5%	U	—
	Tank sludge; 55-gal. drum	NaI, 3 by 3 in. scan	0 to 15	5	<16% at 0.9 g	3.5%	U	—
	Saw sludge; 1-gal. can	NaI, 3 by 3 in. scan	0 to 100	1.7	13% at 2.1 g 4.4% at 33 g	8.6% at 5 g 5.3% at 100 g	U	—
	Saw sludge; 4-L bottle	NaI, 3 by 3 in. scan	0 to 150	1.7	—	8.9% at 5 g 4.2% at 150 g	U	—
	CUNO air filter 55-gal. drum	NaI, 2 by 2 in. scan	0 to 10	1	13% at 2.4 g	2.9% at 7.2 g	U	—
	HEPA filters; 12- by 12- by 24-in. box	NaI, 3 by 3 in. scan	2 to 11	2	—	1.3%	U	—
	Insolubles, ash; 24-in diameter pan	NaI, 3 by 3 in. scan	0 to 200	1	3.3% at 80 to 110 g	11%	U	—
	Laundry; 55-gal. drum	NaI, 2 by ½ in. scan	—	1	<24%	1.7% at 9 g	U	—

Note—See footnote at end of table.

Table 5.2 Summary of performance: standards compensated gamma-ray assay (Cont'd)

Material	Matrix and Container	System	Calibrated Range (g SNM)	Assay Time (min)	Performance (% RSD) Random Error	Performance (% RSD) Systematic Error	Source[a]	Ref.
LEU <5% ^{235}U	Combustible; 25- by 38- by 18-in. box	NaI, 2 by 1 in. scan	0 to 172	4	1.5% at 21 g	<28% at 92 g	U	—
	Combustible 9- by 18- by 18-in. box	NaI, 2 by ½ in. scan	0 to 22.5	2	3.3% at 22 g	2.1% at 1 g	U	—
	Calcined material; 5-gal. pail	NaI, 2 by ½ in. scan	0 to 38	1	13% at 2.9 g 12% at 38 g	9.6% at 3.1 g 17% at 42 g	U	—
	Calcined material; 5-gal. fiberpak	NaI, 2 by ½ in. scan	0 to 12	1	14% at 0.80 g 6.6% at 12 g	2.9% at 0.69 g 8.6% at 10 g	U	—
	Noncombustible; 9- by 18- by 18-in. box	NaI, 2 by ½ in. scan	0 to 10	2	23% at 0.75 g 8.0% at 10 g	2%	U	—
	Noncombustible; 2-qt polyethylene bottle	NaI, 2 by ½ in. scan	0 to 10	1	12% at 0.87 g 8.0% at 10 g	2.9% at 0.77 g 8.6% at 8.7 g	U	—
	HEPA filter; 12- by 24- by 24- in. box	NaI, 2 by ½ in. scan	0 to 10	2	11% at 1 g 1.6% at 10 g	0.42%	U	—
	Residue; 2-qt polyethylene bottle	NaI, 2 by ½ in. scan	0 to 15	1	6.6% at 1 g 9.0% at 15 g	2.2% at 0.95 g 7.1% at 14 g	U	—
	Laundry; 55-gal. drum	NaI, 2 by ½ in. scan	0 to 6	1	4.3% at 6 g	1.6% at 6 g	U	—

Note—See footnote at end of table.

Table 5.2 Summary of performance: standards compensated gamma-ray assay (Cont'd)

Material	Matrix and Container	System	Calibrated Range (g SNM)	Assay Time (min)	Performance (% RSD)		Source[a]	Ref.
					Random Error	Systematic Error		
	Laundry; 55-gal. cardboard drum	NaI, 2 by 1 in. scan	0.25 to 8.0	3	6.3% at 2.7 g	6.9% at 2 g 8.2% at 6.9 g	U	—
	Combustible; 55-gal. drum	4 NaI, 2 by 1 in.	2 to 30	3	20% at 2.0 g 1.8% at 32 g	10% at 2 g[b] 3.4% at 32 g[b]	U	—
	HEPA filter 2- by 2- by 8-in. box	4 NaI, 2 by 1 in.	1 to 33	3	10% at 2.0 g 1.2% at 32 g	7.5% at 2 g[b] 4.7% at 32 g[b]	U	--
HEU in mixed oxide fuel; >90 ^{235}U Pu : U = 1:1	Combustible; 5-gal. bucket	Ge(Li) (9%) scan	0.1 to 15.0	10	11% at 0.1 g 1.8% at 15 g	3.6% at 0.1 g 2.7% at 15 g	U	—
Pu in MOX	Combustible; 5-gal. bucket	Ge(Li) (9%) scan (414 keV)	0.1 to 15.0	10	12% at 0.1 g 3.7% at 15 g	5.8% at 0.1 g 4.5% at 15 g	U	—
25% Pu	HEPA filter; 20- by 20- by 24-in. box	hpGe (8%) scan	0 to 100	16.7	—	1.6% at 53 g	U	—
	HEPA filter; 12- by 12- by 18-in. box	hpGe (8%) scan	0 to 100	16.7	22% at 0.1 g 1.6% at 36 g	2.3 to 6.0% at 21.5 g	U	—
Pu	Waste; 55-gal. drum	NaI, 3 by 3 in. scan	—	18	10 to 50 mg (detection limit)		L	5

Note—See footnote at end of table.

Table 5.2 Summary of performance: standards compensated gamma-ray assay (Cont'd)

Material	Matrix and Container	System	Calibrated Range (g SNM)	Assay Time (min)	Performance (% ESD)		Source^a	Ref.
					Random Error	Systematic Error		
Small sample:								
HEU; > 90% ^{235}U	3-mL liquid; test tube	NaI, well, 3 by 3 in. scan	0.006 to 5.0^c	9	20% at 0.006^c 1.0% at 4.2^c	0.82% at 0.006 to 1 g	U	—
	100-mL liquid; vial	Ge(Li) (6%)	0.005 to 2.0^c	10	9.8%	1.0%	U	—
	In-line liquid: monitor	NaI, 3 by 1 in. scan	2 to 25^c	—	1.0% (accuracy)		L	6
	Residue; test tube	NaI, well, 3 by 3 in. scan	0.005 to 0.58	0.67	2.7% at 0.11 g 1.4% at 0.578 g	0.41% at 0.005 g 1.4% at 0.600 g	U	—
	Liquid: in SS sample cell	NaI, 3 by 1 in. scan	2 to 400^c	—	1.0% (accuracy)		L	6
	250-mL liquid; rectangular culture flask	NaI, 5 by 0.8 in. scan	0.001 to 0.050	—	10% (accuracy)		L	6
LEU and HEU; > 2% ^{235}U	50 mL liquid; vial	NaI, 2 by 2 in. scan	0.2 to 6.0^c	15	0.4% at 1^c	—	U	—

Note—See footnote at end of table.

Table 5.2 Summary of performance: standards compensated gamma-ray assay (Cont'd)

Material	Matrix and Container	System	Calibrated Range (g SNM)	Assay Time (min)	Performance (% RSD)		Source[a]	Ref.
					Random Error	Systematic Error		
Fuel element:	Jacketed ternary alloy (Pu, U, Mo); ZPPR fuel plates 28% and 35% Pu	Ge(Li) scan	–	([d])	0.25%	0.04%	L	7,8

[a] L = literature survey; U = users' survey of production facilities.

[b] Systematic error determined from replicate measurements of physical standards.

[c] mg/mL.

[d] Throughput equals 1000 per month.

ZPPR = Zero Power Plutonium Reactor

channels is a necessity. An oscilloscope is also useful for setting up equipment properly and for monitoring nuclear signals being processed. For process control or inventory applications, a small computer may be used to control the measurements if there are many items to be assayed. Without the computer, electronic component costs range from $5000 to $12,000, including a multichannel analyzer. Computer control adds at least $30,000 to the cost. Complete, portable NaI-based systems designed specifically for SNM assay are also available.

For many applications, automatic scanning of various portions of the assayed item is not necessary. For example, a box may be manually rotated to different configurations between counts. Solution measurements require only a place near the detector to put the sample. For other applications, however, involving the assay of bulky waste and scrap containers or fuel elements, additional mechanical components are required that change the detector-container configuration through rotation and/or translation. In some cases sophisticated computer-controlled detector positioning may be required.

Other hardware items may include printers, data storage media, and lead shielding. More details about passive gamma-ray instrumentation may be found in Reference 9.

Major Sources of Error

Systematic errors in the assay results of passive gamma-ray systems are either the result of variabilities in the material assayed or of changes in the response (count rate per gram of SNM) resulting from changes in the detector or electronics and gamma-ray backgrounds. Systematic changes resulting from variable matrix attenuation or self-absorption in the assayed object are difficult to control or monitor in certain applications of waste and scrap assay.

One major source of error can be from calibration standards in which the particle size and physical configuration of the SNM may not be representative of the objects assayed, even though the chemical form and isotopic composition of the SNM used in preparation of a calibration standard may be identical to that measured in the unknown. If the particle size and distribution of these particles in the standard differ enough from the unknown so that self-attenuation factors differ, then the assay values based on these standards will be biased. More local concentrations of SNM in unknowns (lumpiness) than in standards will lead to increased self-absorption and an underestimation of the SNM content. If physical standards are composed of discrete configurations of SNM, such that the SNM is in high enough concentrations for appreciable self-absorption to occur over that which occurs in the unknowns, then the result based on these calibration standards will be biased high (higher SNM content than the true value).

Measurement Control Requirements

To verify the reliability of the assay system, check sources should be measured on a regular basis to detect gain shifts and changes in detector resolution or efficiency. Possible gamma-ray interferences from contaminated equipment or changes in background level can be detected by periodic background counts. The frequency that background is measured is dependent somewhat on the background variability. If other appreciable sources of radiation are commonly encountered in the vicinity, then background must be measured more frequently. Check sources should be counted at least twice a shift when the system is in use. Check sources can be either actual calibration materials or special sources nominally similar in count rate and radiation characteristics to the items being assayed.

Verification of the accuracy of the measurement should be made on a regular basis by comparison of the gamma-ray assay result with that from chemistry or another NDA method. This procedure can give the most realistic estimate of measurement biases.

Recalibration of the system is necessary if equipment changes are made. If the isotopic composition or matrix type changes such that the response to a given amount of SNM changes, then a new calibration is required.

Data Analysis Requirements

The analysis of the passive gamma-ray data consists of first finding the net area (counts) in the assay peak. This result is transformed into a count rate and then used to obtain total isotopic content by use of a calibration curve or constant. This result, in turn, can be transformed into total elemental content using the available isotopic composition information.

The total peak area generally consists of counts from the full energy gamma-ray peak used for assay and counts from Compton-scattered events. The latter results from higher energy gamma rays scattered from matrix or other material or from Compton-scattering in the detector. To calculate the net counts in the peak that are exclusively from the SNM, background counts are estimated from a straight or curved correction line based on smooth, peakless portions in the neighboring regions of the peak. These corrections can be made with SCAs set around the assay peak and around adjacent part(s) of the spectra (Ref. 9).

Once the best estimate of the net counts in a peak is made, the resultant count rate is then transformed into SNM content using a calibration curve. Counting data from calibration runs are used to define a calibration point or line. A linear or nonlinear calibration curve can be fit to the data using least-squares techniques.

Survey of Selected Literature

Plutonium Waste (Ref. 5)

The material assayed was Pu-contaminated trash, such as paper, cloth, glassware, and filters, sealed in heavy plastic bags and placed in 55-gal. drums for disposal. The isotopic composition was nominally 94% ^{239}Pu and 6% ^{240}Pu.

A lead-shielded, 3-in. diameter by 3-in. long NaI scintillation crystal with an SCA set to encompass the 330 to 440-keV energy interval was used to detect Pu gamma rays. The system output was used to drive a scaler ratemeter. A strip-chart recorder connected to the ratemeter was used to give a visual indication of the localization of SNM. The drums were rotated, and the detector was moved vertically. A 4.3-g ^{239}Pu source in an empty barrel was used for calibration.

The accuracy of the assay was limited by the unknown mass attenuation and geometric uncertainty in the location of the SNM. The sensitivity of the system was estimated to be 10 to 50 mg of Pu for an 18-min scan.

Highly Enriched Uranium Solutions (Ref. 6)

The concentration of HEU in solution in different areas of a process was determined. A description of three assay systems is given in the following paragraphs.

In the first system, uranyl nitrate solutions in a 330-L calibrated tank with concentrations ranging from 2 to 25 g/L were measured with a 3-in. diameter by 1-in. thick NaI detector. The sample cell was installed in a pump line used to mix the tank contents and defined a volume 90 mm in diameter and 2 mm thick. The variation in the 185.7-keV ^{235}U gamma-ray attenuation was <0.5% over this small thickness. A 5-μCi ^{241}Am source was used to stabilize the electronics. Two single-channel analyzers were used to calculate concentrations. One single-channel analyzer was set on the peak, and the other was set above the peak to estimate the amount of background to be subtracted from the peak. The system was used as a process monitor. Two solutions having different concentrations were needed for calibration. The result in grams per liter was displayed visually by a custom designed arithmetic unit. An assay accuracy of 1% (1σ) was reported.

In the second system, uranium process solutions (2 to 400 g/L) in a washable stainless steel sample cell were assayed. Samples were drawn into a 5-mm thick cell, and the 185.7-keV gamma ray was detected with a 3-in. diameter by 1-in. thick shielded NaI detector. The gain stabilization and peak stripping techniques were similar to the previous in-line system. The output was two scaler readings that were converted to grams per liter with a calibration chart. An accuracy of 1% (1σ) was reported.

In the third system, the concentration of U in waste solutions (1 to 50 mg/L) was determined. The solutions were contained in 250-mL plastic containers (commercial culture flasks) with flat sides (7.5 by 10 by 3 cm thick). The 185.7-keV gamma-ray was detected with a 5-in. diameter by 0.8-in. thick, shielded NaI crystal. Gain stabilization and peak stripping were similar to the online system. The output was two scaler readings that were converted to milligrams per liter with a calibration chart. Accuracy of the system was 10% (1σ) at the 1-ppm level. The detectability limit (3σ level above background) was 97 ppb ^{235}U for a 20-min counting time.

Plutonium Fuel Plates (Refs. 7 and 8)

Twelve thousand ZPPR fuel plates, 4.8-cm wide, 0.51-cm thick and ranging from 2.0 to 22.4 cm in length, were measured. The plates were a ternary alloy of Pu (28.3% or 34.5%), Mo (2.5%), and depleted U. The ^{240}Pu isotopic composition was either 11.5% or 25.0%.

A group of up to 53 fuel plates was placed on a table whose *x-y* coordinates could be precisely controlled to 0.001 in. by commands from punched tape. A PDP-8 computer was used to control the scanning table and to collect and analyze gamma-ray data from a shielded, collimated 20 cm^3 coaxial Ge(Li) detector. Each fuel plate on the table was scanned, and the calculated Pu content was obtained by reference to a least-squares linear calibration curve that had been produced from the measurement of five standard plates of different sizes with known ^{239}Pu content. The 414-keV peak of ^{239}Pu and the adjacent higher energy background for each plate were counted. The plates were turned over and recounted. Total Pu content was obtained using chemical isotopic ratios and the ^{239}Pu content. About 1000 plates could be counted each month based on a 40-h week. The 12,000 fuel plates, containing about 3 metric tons of Pu, were assayed in about 1 yr. Backgrounds were found to vary because of differing fission product contamination levels in the alloy and the arrangement and size of neighboring plates on the scanning table.

A group of 344 melts from which plates were later manufactured was sampled, and the samples were chemically analyzed. The average Pu content obtained from chemistry (28.271 %) was lower by 0.049 ± 0.011 % (1σ) from the average gamma-ray assay value. The mean variation of the gamma-ray assay of each melt was ±0.51% (95% confidence limits).

Survey of Production Facilities

Waste/Scrap (U and Pu)

Measurement of waste and scrap by standards-compensated passive gamma-ray scanning is the most common NDA method used. Containers ranging from 1-qt containers to 4- by 4- by 8-ft boxes containing 1 to 250 g of fissile material are measured with this technique. NaI detectors (ranging in size from 2 by ½ to 3 by 3 in.) in combination with one-channel or two-channel analyzers are used to measure the 186-keV gamma-ray peak of ^{235}U or the 384-keV complex of ^{239}Pu. Ge(Li) or hpGe detectors are used to measure groups of gamma rays in the 400- to 450-keV region or the 414-keV gamma ray resulting from ^{239}Pu, for the assay of Pu in mixed (U, Pu) oxides in high-efficiency particulate air (HEPA) filters or combustible waste. The Ge systems are usually used in conjunction with a 4096-channel analyzer.

Cylindrical containers are usually rotated on a turntable to minimize variability in response resulting from SNM location in the container. Rectangular objects are rotated manually, and separate counts are made for each side. To account for vertical variations in SNM location, (1) the detector is usually placed far enough away from the item so that the face of the detector views the entire object; (2) the detector is placed closer, and either the detector or container is moved vertically during scanning; or (3) a fixed multidetector array is set up so that each detector views a different vertical segment of the rotated object.

In standards-compensated assay, as in other NDA methods, two basic approaches are followed in preparing standards used in converting counts per second into grams: preparation of synthetic standards or the use of an actual production item that is subsequently assayed by an independent, traceable technique. Some typical physical standard configurations are shown in Figure 5.2. Two different fabrication techniques are followed in preparing synthetic standards. One technique involves the dispersal of SNM directly into a representative matrix inside the container. The matrix material sometimes consists of actual "cold" material generated by the production process. The other technique uses smaller modular standards. With the modular approach one can simulate the variability in location by varying the position of the "modules." The variability in SNM loading is simulated by using a greater or lesser number of modules. The modules may be the only material placed inside the larger container or may be placed in representative matrix material already there. In the latter case, the matrix material sometimes consists of actual "cold" material generated for production activities.

Some modular forms used currently in 5-gal. or larger containers for standards-compensated gamma-ray assay are the following.

(1) Ribbons (36- by 1-in.) uniformly covered with HEU material, inside tubes
(2) Sheets (8- by 8-in. and 20- by 8-in.), with HEU material sandwiched between two layers of vinyl
(3) Vials of LEU powder
(4) Plastic pipes filled with LEU powder
(5) Sealed plastic gloves filled with mixed oxide (U, Pu) powder

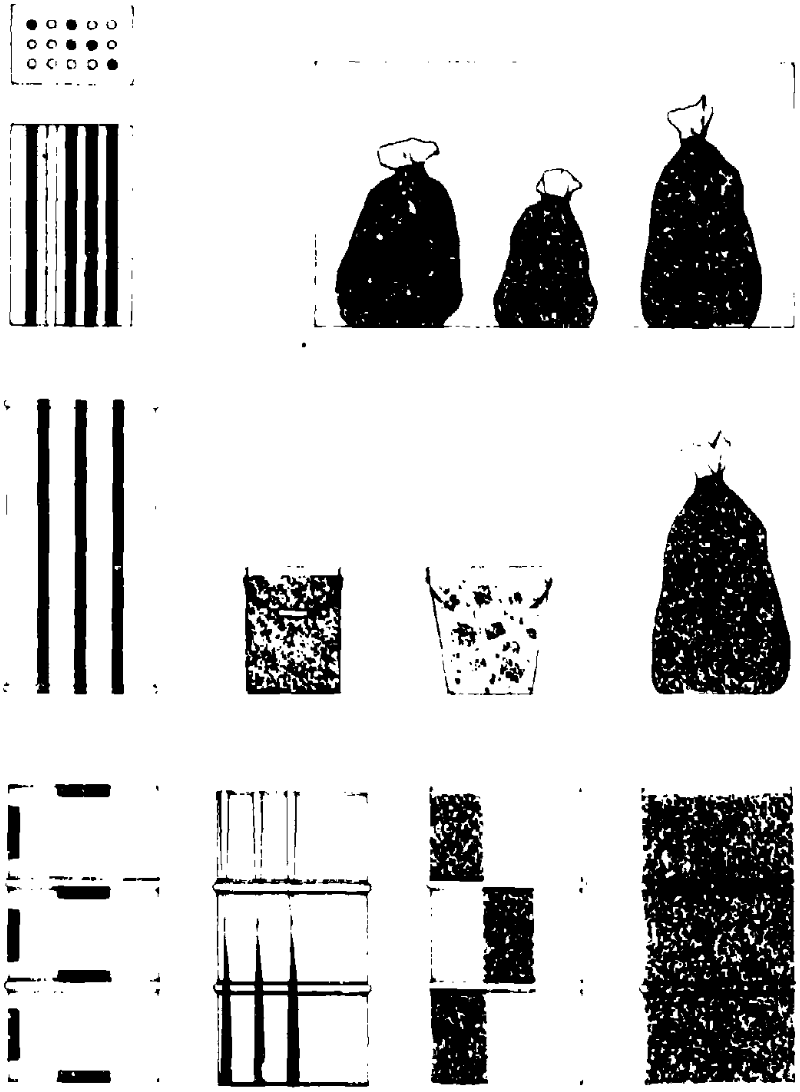

Figure 5.2 Physical standard types.

(6) Plastic jugs with LEU dispersed in powder matrix
(7) Plastic bags filled with representative matrix material and dispersed HEU

Special objects such as HEPA filters may be routinely assayed as a whole. Modular and dispersed standards have been prepared for this type of assayed item. Modular standards consist of vials or tapes bearing SNM placed in holes drilled in standard filters or powder dispersed and sealed inside plastic sheets or plastic pockets attached to the filter face. Dispersed standards consist of powder directly distributed onto the filter face while it is operated.

The most common matrix category that usually has its own set of standards for nearly every facility is combustible waste. Beyond this category, the number of standard sets varies widely from facility to facility. Shown in Table 5.3 are material types measured with passive gamma-ray standards-compensated assay. Each column in this table lists the

Table 5.3 SNM standards used to calibrate passive gamma-rays (standards compensated) system for various scrap and waste categories at production facilities

Facility A	Facility B System 1	Facility B System 2	Facility B System 3
1. Combustible	1. Noncombustible 1	1. Combustible	1. HEPA filter 1
2. Laundry	2. Noncombustible 2	2. Noncombustible	2. HEPA filter 2
	3. Noncombustible 3	3. Laundry	
	4. Combustible		
	5. Calcined residue 1		
	6. Calcined residue 2		
	7. HEPA filter		
	8. Laundry		

Facility C	Facility D System 1	Facility D System 2	Facility D System 3
1. Combustible	1. Residue	1. Scrap waste 1	1. Filters
	2. Combustible	2. Scrap waste 2	
		3. Low Z trash	

Facilities E & F	Facility G	Facility H	
1. Combustible/ noncombustible	1. Sludge 1	1. Combustible	
2. HEPA filters	2. Sludge 2	2. Air filters	
	3. Sludge 3		
	4. Combustible		
	5. Grit blast		
	6. Solution		
	7. Machine chips		
	8. Hard scrap		
	9. Steel jackets		
	10. Ash		

material categories measured by one gamma assay system at a particular facility. Each category requires its own set of physical standards. From this table one can see that each measurement system has a number of standard sets ranging from 1 to 10.

Typically 1 to 4 of these standards are used to produce a calibration curve of SNM loading (grams) as a function of response (for example, counts per second). In some cases a fit is made by visually fitting a linear or nonlinear curve to the data; but usually the response curve is determined by an unweighted least-squares fit of a linear function to the data; functional forms used are $y = bx$ and $y = a + bx$. Some nonlinear forms are also fit in the same manner with functions $\ln y = a + b\ln x$ and $y = ax + bx^2$ being used. For a few facilities a correction is made for attenuation based on the weight of the assayed object, with a mass term directly in the calibration equation or with separate calibration curves prepared for different matrix masses (spanning production values) in the calibration standards. In the latter case interpolation using the mass of the unknown is used to determine the assay value.

The random errors of these measurement systems are plotted in Figure 5.3 for different matrices and measurement systems for U assay. Points connected by lines represent the performance of the same measurement system at two different SNM loadings of the same matrix material. Each of these two loadings were measured by replicate analyses during the same day or within a period of several days. Other random error points in this graph were obtained by duplicate measurements of production items. On this graph one can see that the general trend is toward a smaller relative random error at larger SNM loadings. This is probably the result of better counting statistics and the relatively smaller error in background determination. For the NaI measurement of U, there is a 2% to 25% RSD range in random error for the measurement of less than or equal to 1 g of ^{235}U, with the upper limit decreasing to less than 10% at 5 g, and to less than 5% at 20 g. Typical measurement times ranged from 1 to 5 min per container. The same trend is seen with Ge detectors, with random errors of 12.5% and 22.0% reported for items containing 0.1 g of Pu, decreasing to 3.7% at 15 g, and 1.6% at 36.3 g of contained Pu with measurement times ranging from 10 to 20 min.

The method used to calculate systematic error varies somewhat from facility to facility. Calibration error is, in some cases, equated with systematic error. (See Ref. 10.) Shown in Figure 5.4 is a histogram representing the magnitudes and ranges of systematic errors for U assay calculated in this manner. These range from less than 0.5% to 28% RSD. Systematic errors for the Ge-based system range from 1.5% to 6.0% RSD. In other facilities the shift in an average count rate of a standard is treated as a bias, and the uncertainty in this shift is treated as the total systematic error for the system. The standard or standards in this case are typically

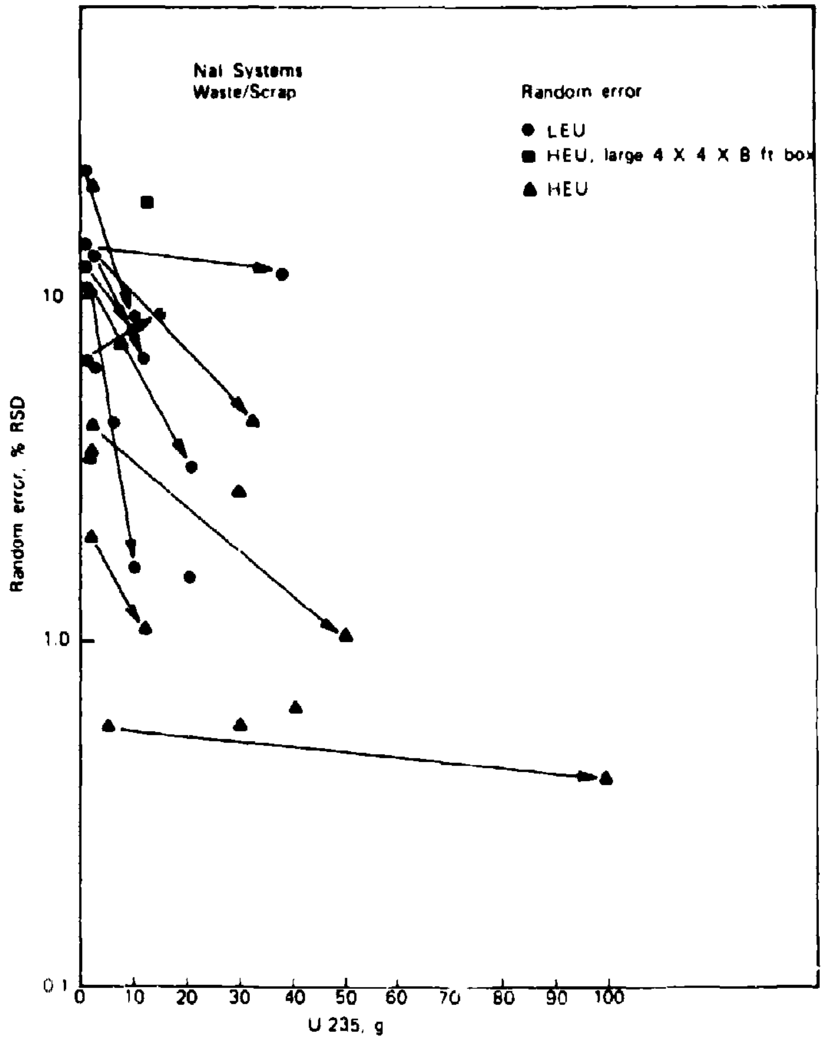

Figure 5.3 Random error performance of various NaI assay systems.

one or more of the calibration standards or a special counting standard. The working standards are usually measured at least twice a week and often more frequently.

A regularly scheduled verification of assay results is normally not performed (with some exceptions) for U assay. Calorimetry, however, has been used for measuring the Pu content of scrap and waste containers to detect any bias in the gamma-ray result.

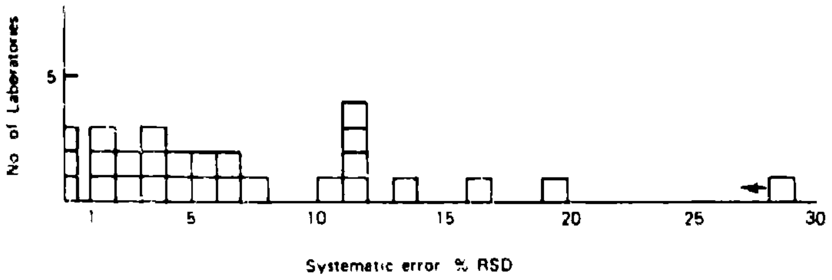

Figure 5.4 Systematic (calibration) error for U in scrap/waste.

Systems of the NaI type have been in operation continuously from 5 to 20 yr at various facilities and have proven to be reliable pieces of hardware. Germanium systems have not been in operation for as long. In some cases they have shown a similar reliability, but, in others, shifts in detector efficiency have been noted.

Data analysis requirements of these systems are minimal; the most complicated calculations required are least-squares fitting of a calibration curve. Determination of the net peak area is obtained by subtracting a background count from the assay count or using a contiguous flat region of the pulse-height spectra for a background subtraction. For most facilities, there are no gamma-ray sources acting as interferences in this assay; however at some facilities, varying background from the presence of other SNM, high count rates from the ^{241}Am present in Pu, and Th gamma-ray interference with a ^{235}U assay peak were some problems that were noted and dealt with.

Setup and subsequent monitoring of these systems are usually performed by personnel with at least a bachelor degree in physical science or engineering. Statistical analyses of the data are usually performed by the facility statistician.

Small Samples

The assay of small liquid and solid samples using passive gamma-ray techniques has been used for accountability purposes at several facilities. The measurement systems consist of a shielded detector, amplifiers, and single channel or multichannel analyzers. These systems have been in use from 6 to 20 yr in various facilities and have been used for process monitoring as well as for accountability measurements.

Solutions of HEU samples with volumes ranging from 3 to 100 mL and concentrations ranging from 0.005 to 5.0 mg/mL have been assayed. Both NaI and Ge(Li) detectors have been used to measure the 186-keV gamma-rays of ^{235}U. Samples were measured either in a test tube placed inside a well counter or in a vial on the detector. In other cases solution samples were either process solutions with concentrations adjusted into the calibrated range or samples resulting from direct dissolution by HNO_3 or via $K_2S_2O_7$ fusion. In one facility, solid samples containing up to 0.6 g of HEU in process residues have also been analyzed similarly.

Standards for these systems are synthetic; known amounts of U compounds are mixed into a representative matrix for the solid samples or dissolved for the liquid samples. The ^{235}U concentration range spans expected production ranges. Five or six calibration standards of different concentrations were prepared for the liquid samples. In one facility separate sets of standards were produced for liquid samples prepared by simple dissolution and by dissolution via $K_2S_2O_7$ fusion. Thirty-five calibration standards composed of different combinations of weight and SNM content were used for a small solid-sample application.

Data collected for assay for these systems generally consisted of gross and background counting data for samples and standards. The total times apportioned to each of these counts differed from facility to facility. Total assay time for liquids ranged from about 10 to 14 min per sample. Standards are measured at least daily when the system is in use, and the results are used to demonstrate measurement control or for renormalization. For some systems one standard is measured for every unknown.

Random error estimates for these systems show the expected behavior for fixed counting times: smaller random errors are observed for the higher concentrations. This trend can be seen in Figure 5.5 where random error data from a solution assay system are plotted along with results from a solid assay system. The random error estimates connected by lines are those from triplicate measurements of each calibration standard taken every week for a total of 8 weeks; both the within-week and total overall variations are plotted in this figure. The total ^{235}U masses plotted here for this set of data are the contents of 3-mL aliquots with concentrations ranging from 0.006 mg/mL to 1.0 mg/mL.

The systematic (calibration) error for the solid sample system was calculated for the functional form $x = ay + by^2$, where x = grams of ^{235}U and y = counts/s, and ranged from 0.41% at 0.005 g ^{235}U to 1.4% at 0.580 g ^{235}U. The systematic error for the solution assay system, the random error of which is plotted in Figure 5.5, was 0.82% for the range 0.006 to 1.0 mg/mL. The functional form used for the calibration curve for that system was $y = ax$.

5.2.1.3 Transmission-Corrected Assay

Description of Method

One of the major sources of uncertainty in the assay of SNM is the amount of attenuation of the SNM gamma-rays by the matrix materials. The loss in gamma-ray intensity can be corrected by measuring the change

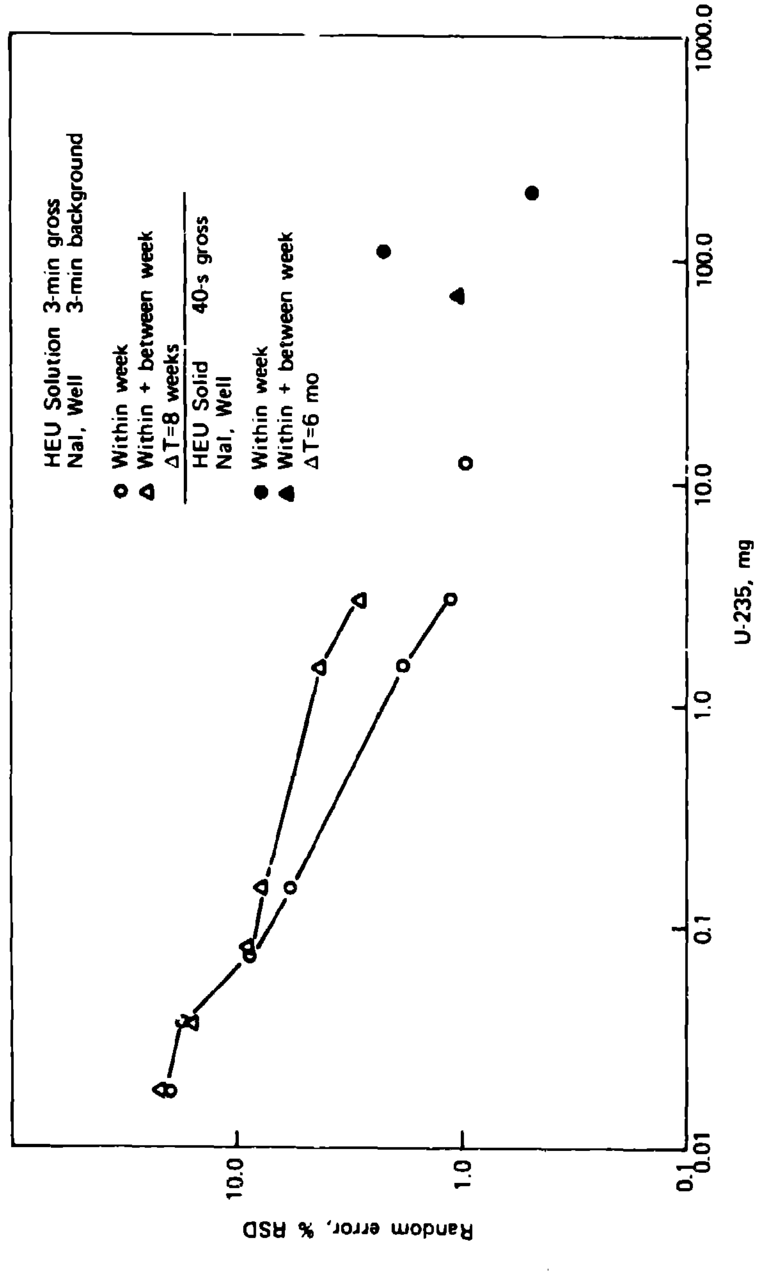

Figure 5.5 Random error (small sample systems).

in transmission of gamma rays through the sample from an external source with energies close to that of the characteristic gamma ray. Table 5.4 lists some transmission sources that may be used. For some applications, a U or Pu source similar in isotopic composition to the material assayed may be used for a transmission measurement. In this case, the sample is counted with and without the source.

Table 5.4 Sources for transmission corrections[a]

Isotope Assayed	Gamma Rays (keV)	Transmission Source	Gamma Rays (keV)
^{235}U	185.7	^{169}Yb	177.2, 198.0
^{238}Pu	766.4	^{137}Cs	661.6
^{239}Pu	413.7	^{75}Se	400.1

[a] From Ref. 9.

The transmission-corrected assay is based on two assumptions. The first is that the matrix material is homogenous, either throughout the entire sample or in increments when segmented scanning is used. The second assumption is that the SNM is sufficiently dispersed as small particles so that gamma-ray self-attenuation in the particles is negligible. Even with these restrictions, the transmission-corrected assays will often be more accurate than the standards-compensated assay for many applications because corrections for matrix attenuations are made for every measurement. Thus, corrections for variabilities in matrix absorption unaccounted for by the physical standards can be made, leading to more accurate assay results.

If more than one measurable gamma ray is emitted by the SNM, then ratio(s) of the gamma-ray intensities may be used to flag excessive matrix or self-absorption conditions. In such cases, there will be an increased absorption of the lower energy gamma ray over what is otherwise expected for a particular sample type.

If the average *Z* of a particular segregated matrix material is known, then the ratio of gamma rays may be used to correct for the loss in gamma intensity. This is known as the differential absorption correction technique (Ref. 11).

As with standards-compensated assays, samples may be rotated and translated past the detector and source, either continuously or in segments, to reduce the variation in assay because of inhomogeneous distribution of the SNM in the container. A segmented scan, that is, vertically scanning the sample by increments, allows each increment of the sample to be corrected for attenuation. A more accurate assay, depending upon the inhomogeneity of the sample, will result from segmented scanning. References 9, 12, and 13 give detailed explanations of the segmented gamma-ray scanning technique.

Scope of Applications

This technique can be used to determine ^{235}U, ^{238}Pu, ^{239}Pu, and ^{241}Pu. The isotope ^{240}Pu is difficult to assay by gamma-ray methods because of the low specific activity of its gamma rays, and ^{242}Pu cannot be assayed because it emits no useful gamma rays.

Various forms of scrap and waste have been assayed by this technique with sample sizes ranging from 1 qt to 55 gal. SNM has been measured in various kinds of containers such as cans, barrels, and cardboard boxes. The smaller containers have been assayed for materials with higher matrix attenuation resulting from higher density and/or higher average atomic numbers. Transmission-corrected assays can be used for any sample for which the attenuation of the transmitted gamma ray is not too severe. Assays based on a transmission as low as 0.2% are possible, but 1.0% transmission is a more practical limit. Samples expected to contain less than 1 g of ^{235}U or ^{239}Pu should not be measured with the segmented scanning technique because of the decreased sensitivity of the method (Ref. 12).

Solutions may also be analyzed using transmission-corrected assay. Small samples (10 to 25 mL) of U nitrate (^{235}U concentration range of approximately 1 to 50 g/L) and Pu nitrate (^{239}Pu range of approximately 0.1 to 500 g/L) have been assayed using this technique.

The differential-absorption technique is applicable to the assay of Pu in combustible waste with a density of <0.3 g/cm^3 or in residues at 1.0 g/cm^3 in a container less than 12 cm in diameter (Ref. 9). It has been used for the assay of bottles of Pu nitrate (100 to 250 g/L).

Summary of Performance

Table 5.5 summarizes the performance of some different transmission-corrected gamma assay systems that are used for accountability measurements or are quoted in the literature.

Equipment

Although NaI detectors were used in earlier transmission-compensated systems, Ge detectors with their better energy resolution now predominate. The Ge detectors simplify the separation of the transmission-source gamma rays from those of the SNM and reduce spectrum-stripping uncertainties.

A regulated high-voltage supply, preamplifier, and associated signal-processing electronics are required. A small computer can be used for the data analysis and for mechanical control of the sample rotator and translator, greatly simplifying the operation of the entire system. Radioactive sources are used for the transmission correction and also for dead time and pulse pileup corrections.

Table 5.5 Summary of performance: transmission-corrected assay

Material	Matrix and Container	Measurement System	Calibrated Range (g SNM)	Assay Time (min)	Performance (% RSD)		Source^a	Ref.
					Random Error	Systematic Error		
HTGR, 93% ^{235}U (186 keV)	UO$_2$, ThO$_2$, graphite; 2-L	SGS (GeLi)	0 to 50	9	6.2	0.7	U	—
			6 to 60	10 to 12		1.2	L	4
	UO$_2$, ThO$_2$, graphite; 5-gal.	SGS Ge(Li)	0 to 50	9	2.4	5	U	—
	Waste, low Z; 55-gal	SGS Ge(Li)	0 to 30	23	5.1	4.4	U	—
			30 to 100	23	2.2	0.5	U	—
Pu (413.7 keV)	Ash; 1-gal.	SGS Ge(Li)	40 to 400^b	5	2% (accuracy)		L	15
	Fluorides, and oxides; 1-gal.	SGS Ge(Li)	24 to 500^b	5	4% (accuracy)		L	15
PuO$_2$ in MOX (413.7 keV complex)	Combustible; 4-L	SGS Ge(Li)	4	—	2.5% (accuracy)		L	16

Note—See footnote at end of table.

Table 5.5 Summary of performance: transmission-corrected assay (Cont'd)

Material	Matrix and Container	Measurement System	Calibrated Range (g SNM)	Assay Time (min)	Performance (% RSD) Random Error	Performance (% RSD) Systematic Error	Source[a]	Ref
Pu (384 keV complex)	Ash and graphite; 4-L	NaI	10 to 700	3.3	< 16	<14 (bias)	L	17
Pu	Pu nitrate ash leach solution: 40-mL	Ge(Li)	0.5 to 5.0[c]	33	0.5[d]	1.3	L	18
			Differential Absorption					
Pu (129.3 and 413.7 keV)	Solution; 10-L	Ge(Li)	100 to 250[c]	17	<2	<5	L	11

SGS = Segmented gamma scanner.

[a] L = literature survey; U = users' survey of production facilities.

[b] Actual content range.

[c] Grams per liter.

[d] For greater than 1 g/L.

Figure 5.6 is a photograph of one of several commercially available Segmented Gamma Scanner (SGS) systems. The cost of these systems ranges from $60,000 to $100,000. A photograph and a schematic of a solution assay system designed for the assay of aqueous Pu samples in a glovebox are shown in Figures 5.7 and 5.8 (Ref. 18). A similar system has been developed for U solution assay (Ref. 19). Costs for these systems range from $40,000 to $100,000. Where a less sophisticated system not requiring a small computer for analysis and control can be used, the cost will be $20,000 to $40,000 less.

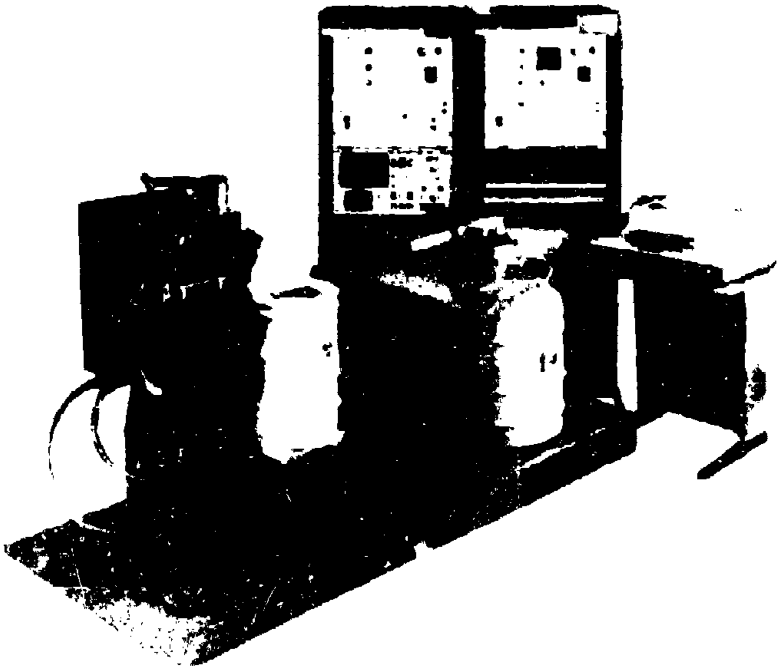

Figure 5.6 Segmented gamma scanning system. (Photograph courtesy of Canberra Industries, Inc.)

Major Sources of Error

A major source of error is the presence of nonuniform, lumpy distributions of the SNM in the container such that source self-attenuation effects bias the result. The presence of unknown amounts of medium- to high-Z materials such as Pb or Fe in a nonuniform distribution can lead to possible error. For transmissions below 10%, the effect of small-angle Compton scattering or "buildup" is a problem for NaI detector systems.

Figure 5.7 Plutonium solution assay system. (Photograph courtesy of Los Alamos National Laboratory.)

Using an SGS, the transmission will be overestimated if the sample is thinner than a one segment interval.

Measurement Control Requirements

The standards used for calibrating the transmission-corrected assay systems must be developed by the user for a particular application. The standards should consist of well-determined amounts of SNM distributed in a matrix similar or identical to that of the samples to be measured and covering the range of SNM amounts anticipated with at least four distinct SNM masses. The frequency of remeasuring working standards used to monitor the stability of the system is somewhat dependent on the frequency of assays and environmental factors that could affect assay results. A working standard should be counted, however, at least twice per shift while the system is in use. Recalibration should be implemented if equipment parameters (such as peak-fitting software and gain settings) are varied or if the detector-to-sample configurations are changed. New physical standards will need to be fabricated if changes have occurred in properties of the assayed material that will affect the accuracy of a result.

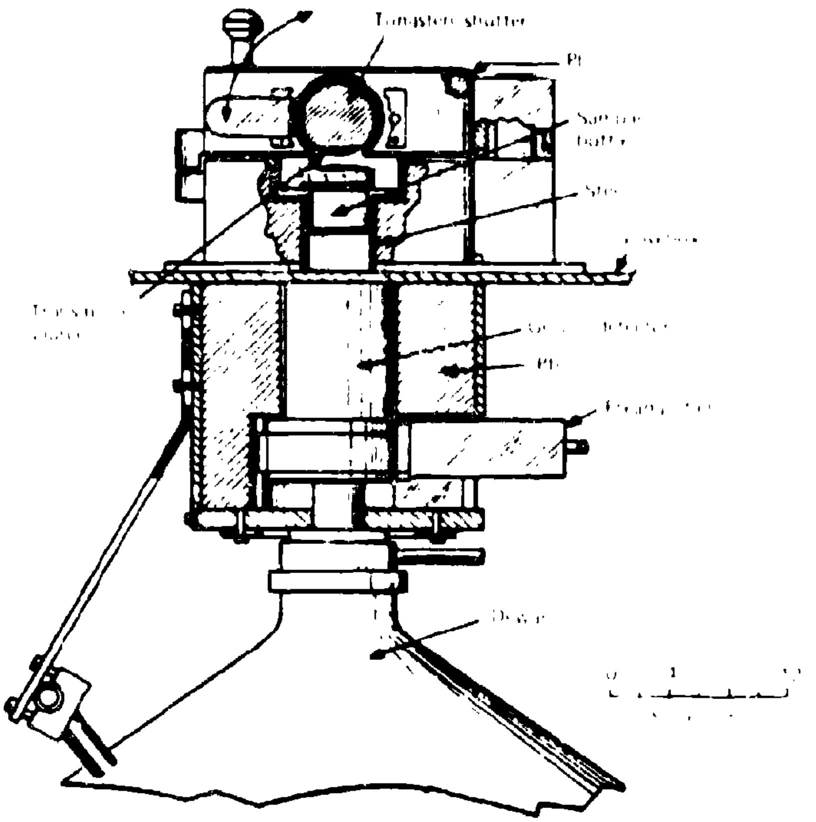

Figure 5.8 Schematic of the plutonium solution assay unit showing the sample in the position for counting. (Figure courtesy of Los Alamos National Laboratory.)

Such changes would include matrix form and shape, size of container, SNM particle size, or isotopic composition. Unknown samples will have to be repackaged if transmissions are too low or the SNM content is above the calibrated range.

Data Analysis Requirements

If a sample is placed between a gamma-ray source and a detector, the ratio of the intensity I of gamma rays that have passed through the sample to the intensity without the sample present I_0, is the transmission T of the sample; that is

$$T = \frac{I}{I_0} \tag{5-1}$$

An estimate of the fraction of the *internal* gamma rays emitted by SNM absorbed by the matrix can be calculated by measuring the transmission of an *external* gamma ray through a sample. The measured count rate, CR, is multiplied by the appropriate correction factor, CF, and the resultant corrected count rate, CCR, is the one that would have been detected if there had been no matrix absorption. Some correction factors are

$$\mathrm{CF} = \frac{\ln T}{1-T} \tag{5-2}$$

for a slab-shaped object and

$$\mathrm{CF} = -\frac{(\pi/4)\ln T}{(1-T)^{\pi/4}} \tag{5-3}$$

for a cylindrical object. A discussion of the derivation of these approximate forms and an estimate of the errors involved in their use may be found in References 3, 9, and 20.

The count rate for each physical standard CR_s with a known SNM mass M_s is multiplied by the appropriate correction factor CF_s based on a measured transmission through the standard. The calibration constant for a standard K_s may be calculated as shown in Eq. (5–4).

$$K_s = \frac{\mathrm{CR}_s \cdot \mathrm{CF}_s}{\mathrm{M}_s} \tag{5-4}$$

In the calculation of the correction factor, the transmission T is assumed to be measured at the gamma-ray energy used for the assay. If the transmission gamma-ray energy is far enough removed from that used for assay, so that the absorption coefficient differs significantly, then a correction to the measured transmission must be made to estimate the transmission at the assay energy. This correction is given by

$$T_a = T_t^{\alpha} \tag{5-5}$$

where a refers to the SNM gamma-ray energy, t to the transmission gamma-ray energy, and α is the ratio of mass absorption coefficients μ_a/μ_t.

Some computer-based transmission-compensated assay systems (such as the one shown in Figure 5.6) have the capability of evaluating Eqs. 5–1 through 5–5 automatically for each segment of an assayed object and, hence measuring the SNM mass in all segments.

For the differential absorption technique where one uses two gamma rays from SNM in the sample, a correction factor of the form

$$CF = \left(\frac{I_1/I_2}{I_1'/I_2'} \right)^{\mu_2/(\mu_1 - \mu_2)} \qquad (5-6)$$

can be used. I_1 and I_2 represent measured intensities, I_1' and I_2' represent intensities from a sample with negligible attenuation, and μ_1 and μ_2 represent the estimated mass absorption coefficients of the matrix material. As a corollary of this technique, one can use the measured ratio as an indicator of excessive self-absorption in the SNM material itself by noting whether the observed ratio differs significantly from the measured ratio due to standards. Further discussions about this technique may be found in References 9 and 11.

Survey of Selected Literature

High-temperature Gaseous Reactor (HTGR) Scrap (Refs. 14 and 21)

The material assayed consisted of HTGR fuel scrap, UO_2 (93% enriched U), and ThO_2 in graphite flour. The mass of ^{235}U ranged from 6 to 60 g.

A segmented gamma-ray scan system with a Ge(Li) detector was used for ^{235}U assay based on the 186-keV gamma ray. The data were transmission-corrected with a 20-mCi ^{169}Yb source and corrected for electronic dead time and drifts with a 10-μCi ^{57}Co source. In-house standards of 6 to 60 g of ^{235}U were used for calibration. The scrap was contained in 2-L polyethylene bottles, and 10- to 12-min counting times were used.

The systematic (calibration) error of the assays was 2.5% (95% confidence level).

Plutonium Incinerator Ash and Scrap (Ref. 15)

The material assayed consisted of Pu (94% ^{239}Pu, 6% ^{240}Pu) in 15-cm diameter by 25-cm high metal cans as (1) incinerator ash with 40 to 400g Pu per can (15 cans scanned) and (2) "dirty" fluorides and oxides with 24 to 500 g of Pu per can (16 cans scanned).

A SGS system with a Ge(Li) detector was used for ^{239}Pu assay. The cans were assayed with 5-min counts per can. The 401-keV gamma ray from ^{75}Se was used for transmission measurements, and the ^{239}Pu 414-keV gamma ray was used for assay. The single standard used was considerably different in size and matrix.

In the ash-sample assay, a bias of +2% was noted relative to a calorimetric assay, probably resulting from the difference between the samples and the standard. The accuracy of the measurements was 4% (2 σ). In the assay of fluoride and oxide samples, an accuracy of 8% (2 σ) was obtained with a ~4.3% average bias between the gamma-ray result and calorimetry. An additional 22 cans of oxide and green cake had unmeasurably low transmissions.

Plutonium in Graphite and Ash (Ref. 17)

The material assayed consisted of known amounts of Pu mixed with an ash and graphite matrix in 1-gal. containers. Plutonium contents ranged from 10 to 700 g (94% ^{239}Pu, 6% ^{240}Pu).

A 2-in. diameter by 2-in. high NaI detector and SCA were used to measure the 384-keV complex of ^{239}Pu. A 200-g PuO_2 gamma-ray source was used for the attenuation measurements. Two 100-s scans were performed, with and without the PuO_2 source. The gross neutron count from Pu was simultaneously recorded with four ^{3}He detectors. Each item was rotated at 20 rpm and translated simultaneously. This passive gamma-ray system is called the "helix counter."

For 15 graphite and ash standards, each measured five times and each containing 10 to 700 g of Pu, a precision of <16% and a bias of <14% were obtained.

Plutonium in Combustible Waste Standards (Ref. 16)

The material assayed was 12 mixed-oxide (2.9% or 3.9% Pu) standards fabricated by distributing known amounts of mixed-oxide powder in 1-gal. cans filled with shredded tissue. The oxide components consisted of natural U and Pu with 80% to 90% ^{239}Pu. SNM content of the cans ranged from 0.8 to 4.2 g ^{239}Pu.

The standards were measured with a SGS system that used a Ge(Li) detector. The 413.7-keV gamma ray from ^{239}Pu was used for the assay, and a ^{75}Se source was used for the transmission correction. The calibration standard was 50 g of Pu mixed in MgO sand. Two of the standards were measured with a segmented scan, the others with an open scan.

The total ^{239}Pu content of the 12 cans was assayed at 36.5 g. The stated value was 37.2 g. The measurement accuracies were 5% at 2 σ.

Plutonium Leach Solutions (Ref. 18)

Eighteen Pu (94% ^{239}Pu, 6% ^{240}Pu) ash/leach solutions with Pu concentrations ranging from 0.5 to 5 g/L were measured. The sample volume was 40 mL.

A Pu solution assay system was used with a Ge(Li) detector and a minicomputer. Simultaneous assays of ^{239}Pu were made using the 129.3- and 413.7-keV gamma rays and of ^{241}Pu using the 148.6- and 208.0-keV gamma rays. A 20-g, 25-mm diameter, Ni-plated Pu metal disk was the transmission source, and a ^{109}Cd source was the count rate correction source (the ^{109}Cd, 88.0-keV gamma ray was used). The ^{109}Cd, 88.0-keV gamma ray and the ^{239}Pu, 413.7-keV gamma ray were used for a digital stabilization of the energy scale to a few hundredths of a keV. A standard solution was counted daily. A background run was taken once a week, and a count of the transmission source without a sample was taken daily to correct for ^{109}Cd decay ($t_{1/2}$ = 453 days). Samples were counted with and without the transmission source for 1000 s each.

The precision, determined by multiple runs on standard solutions, was about 0.5% for Pu concentrations greater than 1 g/L. To test the accuracy of the assay, the results from the solution assay and mass spectrometry were compared for the 18 ash/leach solutions. The average ratio of the solution assay to mass spectrometry was 0.995 ± 0.013.

Plutonium Nitrate Solutions (Ref. 11)

A series of fifteen 10-L bottles of Pu nitrate (86% ^{239}Pu, 11.6% ^{240}Pu) in nitric acid solution were measured. The Pu concentration was 100 to 250 g/L. The containers were in stainless steel jackets (1.9 or 3.4 mm thick).

A differential absorption technique was used for determining Pu using the 129.3- and 413.7-keV gamma rays from ^{239}Pu. The measured ratio of these gamma rays was used directly as an estimator of the Pu concentration. A Ge(Li) detector and 1000-s counting times were used.

The value of the concentration determined from the assay was compared to the value from chemical analysis for each of the 15 bottles. They agreed within 5%. The precision (reproducibility) of the measurement was better than 2%.

Survey of Production Facilities

Transmission-corrected measurements of scrap and waste are made at several facilities for accountability purposes. At one of these sites HEU in the form of ThO_2/UO_2 mixed with graphite in 2-L and 5-gal. containers has been assayed with an SGS using the 186-keV gamma ray of ^{235}U. The system was calibrated with standards ranging from 2 to 50 g for each of the container types. In addition, the system has been used to assay combustible and noncombustible waste in a 55-gal. barrel and is calibrated up to 100 g of ^{235}U. The system (Canberra 2220BC) is a completely automated, computer-based gamma-ray assay system with two turntables to accommodate the container sizes. Two 10% Ge(Li) detectors are used, one for barrels, and the other for smaller containers. The transmission source was ^{169}Yb.

Based on 16 duplicate measurements of standards over a 2-month period, random errors of 6.2% and 2.4% were obtained for the 2-L and 5-gal. $(U,Th)O_2$ graphite samples, respectively. Systematic errors of 0.7% and 5.0% were also calculated for the container and matrix combinations. Random and systematic errors were also calculated for the assay of low-Z waste in 55-gal. drums for two different ranges of SNM content. For the 0- to 30-g ^{235}U range, a random error of 5.1% and a systematic error of 4.4% were determined. For the 30- to 100-g range, the random error was 2.2%, and the systematic error was 0.5%. The systematic errors were calculated from uncertainties in the calibration curve, $y = a + bx$. The curve was fit to the data using an unweighted least-squares fit. These errors were estimated by 560-s counts of the smaller containers and 1400-s counts of the 55-gal. barrels. Typical transmissions encountered ranged from 0.05 to 0.50.

For the smaller containers, synthetic standards were prepared using known amounts of U/Th oxide mixed with carbon, trichloroethane, and ethyl cellulose. The latter two compounds harden and hold the remaining material in place. This standard mixture was placed directly in the 2-L container and in 1-gal. cylindrical cartons for use as modules in a 5-gal. pail. Another set of standards was prepared in 55-gal. drums using this binder method. Two standards from each of the three sets were measured each week (in duplicate). Data analysis was done automatically with this assay system; the assay value for each segment and the total drum was reported.

5.2.1 ma-Ray Absorptiometry

Descri of Method

Gamma-ray absorptiometry is used to determine the concentration of SNM in solutions. A beam of gamma rays from a single isotopic source is passed through a sample and attenuated. The amount of transmission is related to the SNM concentration through

$$\frac{I}{I_0} = e^{-\mu\varrho x} \qquad (5-7)$$

where I is the transmitted intensity, I_0 is the beam intensity with no SNM present, μ is the SNM mass absorption coefficient (in square centimeters per gram), ϱ is the average bulk density in the sample volume (SNM concentration), and x is the length of the interrogated path. This technique assumes that the attenuation caused by the SNM is much larger than that from the matrix material. It is not specific to any SNM; no signature identified with U or Pu is used. If chemical impurities are known to produce

Table 5.6 Summary of performance: gamma-ray absorptiometry[a]

Sample Type	Concentration (g/L)	Sample Size (mL)	Performance (% RSD) Random Error	Systematic Error	Bias (g/L)	Ref.
U in aqueous solution	10 to 250	7	0.2 to 1.0	—	—	22
U in hexane	29.4	1	2.3	—	1.8 ± 1.7	23

[a] All data from literature survey.

negligible error, the method may be used for process control or for more accurate assay of aqueous or organic solutions contained in sample cells with dimensions held to close tolerances. A series of calibration standards may be produced with properties similar to those of the solutions to be assayed, with the assay result obtained from the resultant calibration curve.

Scope of Applications

The technique can be used for determining U in aqueous or organic solutions containing less than 100 mCi of gamma-ray activity per liter, with concentrations ranging from 10 to 350 g/L. The technique could also be used for determining Pu. Gamma-ray absorptiometry has also been applied to the measurement of the density of fuel rods and has been incorporated into active assay systems. (See Chapter 6.) Gamma-ray absorptiometry using two separate gamma-ray energies is discussed in Sections 5.2.1.5 and 5.2.1.6.

Summary of Performance

Table 5.6 summarizes the performance of some gamma-ray absorptiometric systems.

Equipment

The equipment needed for this technique consists of an external gamma-ray source, a sample cell, collimators, detectors, and associated electronics. One arrangement that has been developed is shown in Figure 5.9. Americium-241 has served as the gamma-ray source for U assay, but ^{57}Co would be preferable for Pu. Sample cells with dimensions held to close tolerances can be used to hold the solutions. Optical spectrophotometer cells with path lengths of 1 to 10 cm are commercially available and could be used in this application. A thin NaI scintillator (0.5 cm is sufficient for 60-keV gamma rays) can be used to detect the gamma rays, and one or two SCAs are used to obtain peak areas if pulse-height analysis is used. A potentiometric recorder may be used to record phototube current directly.

Major Sources of Error

This method measures attenuation only and is not specific to U or Pu. Large amounts of low-*Z* matrix material, such as nitrate ions, and smaller amounts of high-*Z* matrix material can cause additional attenuation of the gamma-ray beam and lead to an error in the SNM determination; the assay will be biased high. The solution content must be controlled to eliminate these sources of error.

Fission-product gamma rays constitute an interference. The influence of fission-product gamma rays is reduced by the use of a thin NaI crystal, which is less efficient for the detection of the higher energy gamma rays. The sample may be measured with and without a source to determine the effect of the fission-product gamma rays; however, for one system (30 mCi ^{241}Am, 5- by 1-cm NaI detector, 25-mm cell), ^{137}Cs activity as high as 200 μCi/L was estimated to bias the assay result by 1%(Ref. 22). For Pu measurements, gamma-ray interference from Pu and ^{241}Am in process solutions requires a two-step measurement, with and without the transmission source.

Measurement Control Requirements

A series of standard solutions is needed for calibration over the expected range. Standard reference materials should be used to prepare the absorption standards. If extraction from an aqueous solution is required, then the standard solutions should be treated identically to the samples. Chemical procedures for the preparation of the calibration standards are given in Reference 24. The calibration curve is exponential with SNM concentrations as indicated by Eq. 5–7. A linear least-squares fit of the logarithm of attenuation as a function of concentration simplifies the data analysis. The system should be checked regularly with a reference source for PM drift.

Data Analysis Requirements

The data analysis for this gamma-ray absorptiometric technique requires the measurement of a gamma-ray intensity through the sample R_0. This reading can be taken from a current meter or SCA. The gamma-ray reading can be corrected for fission-product Pu or Am activity by measuring the sample without the transmission source R_g. Similarly, the intensity of the transmission source can be measured through a blank solution (without SNM) R_m The concentration is determined from the ratio $(R_0 - R_g)/R_m$ and a previously determined calibration curve.

Survey of Selected Literature

Uranium Solutions (Refs. 22 and 23).

The material assayed was a set of solutions with U concentrations ranging from 10 to 250 g/L in 25-mm long glass cells and containing no fission product activities.

The apparatus shown in Figure 5.9 was used to measure U concentration. The total current from the scintillator (2 by 0.5-in. NaI) PM was used to drive a potentiometer recorder with 0.05% reading accuracy. The variation in 10 average chart readings, each measured over a 2-min period, was

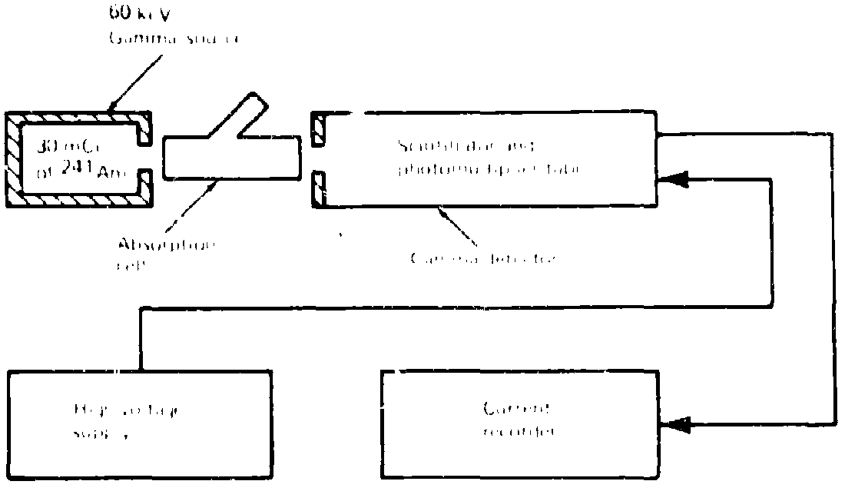

Figure 5.9 Absorptiometer block diagram (from Ref. 24).

used to determine the precision of the system. Precisions from 10 replicate determinations were 0.8% at 10 g/L, 0.2% at 50 and 100 g/L, and 1% at 250 g/L.

Another material assayed was a 0.10 *N* nitric acid solution containing U at a concentration of 30 g/L and potassium dichromate at 7.4 g/L. No fission products were present.

As part of a larger exchange program, a standard solution was sent to another laboratory to test the accuracy of the measurement. The material was measured with apparatus similar to that previously described but with a shorter cell, 12 mm long. The U was extracted into hexane, and a sample of the organic phase was assayed. The measured average value was 29.4 g/L with a precision of 2.3% (1 σ). The difference between the measured and prepared values was +1.8 ± 1.7 g/L (95% confidence level). These data are based on measurement of three samples.

5.2.1.5 Dual Energy Gamma Gauge (DUEGG)

Description of Method

The averge bulk density distribution of SNM-containing samples is determined often by transmission measurement of gamma rays. The fraction of gamma rays transmitted from the interrogated beam (e.g., "good geometry" configuration) is given by $e^{-\mu\rho x}$ where μ is the effective mass absorption coefficient (in square centimeters per gram), ρ is the average bulk density in the sample volume interrogated by the beam (in grams per cubic centimeter), and x is the length of the interrogated path (in centimeters). Thus, if any two factors are known, the third can be determined by the transmission measurement. Transmission measurements are relatively simple, quick, and relatively inexpensive. Gamma-ray transmission can, in some important cases, provide information not only on the average bulk density but also on the composition of the sample. This is based on the fact that the absorption of low energy of gamma rays is a strong function (because of the photoelectric effect) of the atomic number Z of the absorbing element, whereas at high energies the mass absorption coefficient is basically independent of the characteristics of the absorbing elements. Thus, if the interrogated sample is made basically of two components, such as low-Z elements (like C, O, H, and N) and high-Z elements (like U, Th, and Pb), transmission of two different gamma rays can determine the concentrations of these components. The total attenuation of each radiation is given by the exponential relation

$$R_i = R_{i0} \exp[-(w_\ell \mu_{\ell i} + w_h \mu_{hi})\rho x] \qquad i = 1,2 \qquad (5-8)$$

where

R_i = count rate of a source with energy E_i

R_{i0} = count rate of the source with no sample

$\mu_{\ell i}, \mu_{hi}$ = mass absorption coefficients (cm^2/g) of the light and heavy components, respectively, at energy E_i

w_ℓ, w_h = weight fractions of the light and heavy components, respectively.

The two equations for $i = 1$ and 2 can be solved to determine the two unknowns w_ℓ and w_h. The necessary condition for the existence of such a solution is

$$D = \mu_{h2}\mu_{\ell 1} - \mu_{h1}\mu_{\ell 2} \neq 0 \qquad (5-9)$$

This condition states that the Z dependence of the attenuation coefficients for the two selected gamma-ray energies must behave differently; that is, they must be strongly independent. Any measurement error in the DUEGG is amplified by the factor $1/D$.

The sensitivity and accuracy of the DUEGG depends largely on the choice of the two gamma-ray energies and on the composition of the sample.

Scope of Applications

The DUEGG is applicable to measuring the amount or concentration of each component in a two-component sample. The components can be two different elements or a number of elements and compounds that can be grouped into two distinct components based on the average Z. In principle, N components can be measured using N different gamma-ray energies. In practice, however, the method has been applied only to two-component systems.

Though the applicability of the DUEGG should be analyzed separately for each case, generally it will be applicable to two-component systems made of low-Z matrix material, such as C and O or Al and Ca and high-Z heavy metals, such as U and Th. Thus DUEGG can apply to waste, scrap, and product materials. It will also apply to two-component systems made of H, C, N, and O as the low-Z group and Ca and Fe (intermediate elements) as the high-Z group. The DUEGG is applicable also to solutions (aqueous or organic) of U and Pu.

Summary of Performance

One device has been built to measure the amount of low-Z material (C and Si) and high-Z material (Th and U) in HTGR fuel pellets (Ref. 25). The low-Z component was measured with an accuracy of 1.2% (1σ), and the high-Z component was measured with an accuracy of 1.5% (1σ).

Equipment

A DUEGG system consists of two collimated gamma-ray sources viewing either one detector or two separate detectors. If one detector is used, it should have sufficient energy resolution so that the two gamma-ray lines can be measured simultaneously with only slight interference. NaI(Tl) usually has the necessary energy resolution. Single-detector systems are more compact. Two-detector systems require two complete counting setups, each consisting of a detector, preamplifier, amplifier, SCA, and scaler. The physical design of the system should take into account the error amplification that characterizes the DUEGG. The field of view, or the portion of the sample interrogated by the dual gamma-ray beam, has to be constant. The mechanical rigidity of the system is very important.

The estimated cost of a DUEGG system for assay of a gallon-size container is about $15,000 to $25,000.

Sources of Error

The sources of error in the DUEGG method can be clearly identified by a straightforward error analysis of two gamma-ray transmission equations. Such an error analysis shows that generally, if the errors in the attenuation coefficients (calibration errors) are about the same for the high- and low-Z materials, the heavy material component is determined with greater ease and accuracy. This is the case because the high-Z material dominates the absorption at low energies. The light-material component is more susceptible to measurement errors. The largest error components result from the measurements of the transmission of the high-energy gamma rays (random counting error) and uncertainties in the attenuation coefficients of the high-energy gamma rays in the heavy component calibration. Because the attenuation of the high-energy gamma rays is relatively low and no serious limitation on the source strength exists, these errors can be reduced by using properly designed detector and associated electronics for fast counting. The major systematic errors are lack of accurate knowledge of the standards and varying fields of view resulting from vibration or other mechanical deformation. The uncertainty in the standards is translated into uncertainties in the attenuation coefficients.

Measurement Control Requirements

The uncertainties and differences between standards and unknown samples appear as uncertainties in the attenuation coefficients $\mu_{\ell 1}$, $\mu_{\ell 2}$, μ_{h1}, and μ_{h2}. Thus the main measurement control requirement is having well-characterized standards that cover the range of composition expected for the unknown samples. The mechanical construction and configuration of the standards should be very similar to the unknowns.

During the calibration, the attenuation coefficients should be determined precisely (by means of a measurement time longer than for normal measurements of unknowns) to remove any major contribution from counting statistics to the overall uncertainty. The minimum number of standard calibration samples is four, since there are four attenuation coefficients to determine. After establishing the reproducibility of the measurement system, one can monitor performance by repeating the measurement of one standard sample. Typically, standard measurement frequencies of once or twice a day, or once during each batch of unknown samples, were found sufficient.

Data Analysis Requirements

Determination of the masses of the two components involves solving two equations with two unknowns. The solutions are simply

$$w_{\ell}\varrho x = \frac{D_1}{D} \text{ and } w_h \varrho x = \frac{D_2}{D} \qquad (5-10)$$

where D is defined in Eq. (5–9) and

$$D_1 = \mu_{h1} \ln\left(\frac{R_2}{R_{20}}\right) - \mu_{h2} \ln\left(\frac{R_1}{R_{10}}\right)$$

$$D_2 = \mu_{l2} \ln\left(\frac{R_1}{R_{10}}\right) - \mu_{l1} \ln\left(\frac{R_2}{R_{20}}\right)$$

The attenuation coefficients μ_{l1}, μ_{l2}, μ_{h1}, and μ_{h2} are constants. This type of analysis, including the error analysis, can be done either manually, by a programmable calculator, or by an interfaced processor.

Survey of Selected Literature:

Light and Heavy Element Ratio in HTGR Fuel Sticks (Ref. 25)

The material measured was HTGR fuel sticks with C and Si as the low-Z components, and with Th and U as the high-Z component. Because the U had been determined by other means, the primary use of this device was to determine the Th content.

The fuel rods were packed in a hexagonal array containing 150 sticks inside a 6-in. diameter, 2-in. high container. The container was irradiated at an oblique angle to avoid problems with radiation streaming through the spaces between fuel sticks. A wedge was added to correct for different path lengths through different parts of the container. A 5-in. diameter by 3-in. thick NaI(Tl) detector and two sources, ^{133}Ba and ^{60}Co with gamma-ray energies of 0.356 MeV and 1.17 and 1.33 MeV, respectively, were used.

For a 2-min measurement, the heavy component (Th and U) was measured with an accuracy of 1.5% (standard deviation), and the low-Z component (C and Si) was measured to 1.2% RSD. Because the statistical uncertainty (random error) in the measurement was less than 0.25%, most of the error came from the uncertainty in the standards employed. The uncertainty in the attenuation coefficients was estimated to be about 2%.

5.2.1.6 X-Ray Absorption-Edge Densitometry

Description of Method

The X-ray absorption-edge densitometry technique is used to measure U and Pu concentrations in solutions and is relatively free from matrix effects. This method measures elemental and not isotopic compositions. The technique is based on the fact that there is a very large change in the gamma-ray mass attenuation coefficient $\mu(E)$ for an element at energies close to an X-ray absorption edge. Figure 5.10 shows the change in the

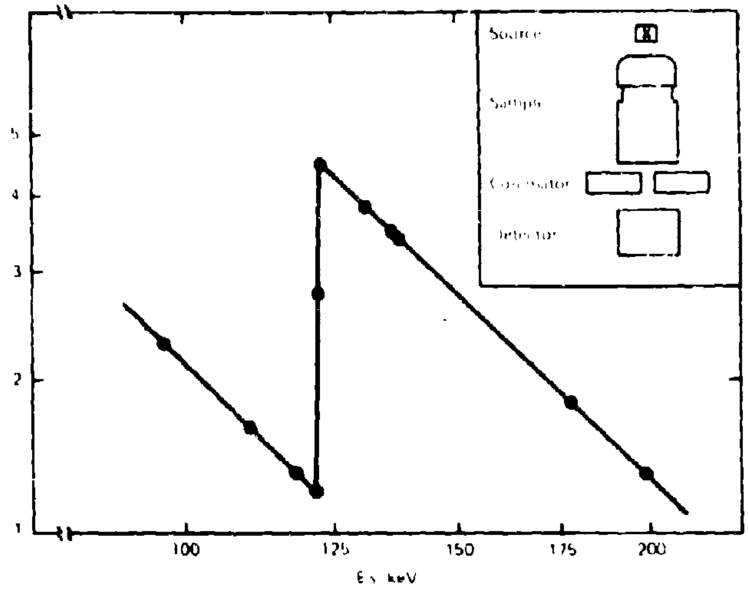

Figure 5.10 Change in mass attenuation as a function of energy across the *K* absorption edge for plutonium (from Ref. 26.)

$\mu(E)$ near 120 keV. By measuring the transmission of gamma rays with energies bracketing the edge closely (within 10 keV for the *K* edge and within 5 keV for the *L* edge), one can calculate the elemental concentration (density) with a result nearly independent of variations in the matrix density.

The transmission T determined by the ratio I/I_0 of gamma-ray intensities with and without the SNM and matrix is

$$T = \frac{I}{I_0} = \exp\ [-(\mu_s\varrho_s x + \mu_m\varrho_m x)] \tag{5-11}$$

where μ_s and μ_m are the mass attenuation coefficients at gamma-ray energy E of the SNM and the matrix, respectively, ϱ_s and ϱ_m are the densities of the SNM and the matrix, respectively, and x is the sample thickness. The absorption-edge densitometry technique requires the measurement of the transmissions for energies above the edge energy E_u and below the edge energy E_l. The ratios of the transmissions yield

$$R = \frac{T_u}{T_l} = \exp[-(\Delta\mu_s\varrho_s x + \Delta\mu_m\varrho_m x)] \tag{5-12}$$

where

$$\Delta\mu = \mu_u - \mu_l \quad (5-13)$$

Figure 5.11 shows the energy dependence of μ for H_2O, Sn, and U. As the difference in energies $E_u - E_l$ about the SNM edge energy is made very small, $\Delta\mu_m$ for the matrix (for example, H_2O or Sn) will become very small, but $\Delta\mu_s$ for the SNM will not because of the discontinuity in μ_s at the edge. For ΔE small,

$$R \cong \exp(-\Delta\mu_s \varrho_s x) \quad (5-14)$$

and

$$\varrho_s \cong -\frac{\ln R}{x\Delta\mu_s} \quad (5-15)$$

so by measuring R and X and knowing $\Delta\mu_s$, one can determine the SNM concentration (density) ϱ_s.

The values of the K and L_{III} absorption-edge energies and the $\Delta\mu_s$ are given in Table 5.7 for U and Pu. Radioactive sources that can be used for the K edge measurements are given in Tables 5.8 and 5.9. The continuous X-ray spectrum from an X-ray machine is used for the L edge measurements because no gamma-ray sources with appropriate energies are available. It might be feasible to fluoresce secondary targets whose K X-ray energies bracket the L_{III} edge, but this approach has not been developed (Ref. 26).

Scope of Applications

The K edge and L edge densitometry methods are used for SNM solutions in the 50- to 500-g/L and 2- to 200-g/L ranges, respectively. The samples should have, for the K edge methods, $\varrho_s x > 0.2$ g/cm^2 and, for the L edge methods, $\varrho_s x > 0.004$ g/cm^2. The sample thickness x is 2 to 4 cm or less for convenient measurements. Simultaneous determinations of U and Pu densities in mixed solutions have been demonstrated for concentrations of 1 to 2 g/L of Pu and 4 to 5 g/L of U.

The use of absorption-edge densitometry has been applied to the assay of SNM contained in ash or fuel plates. Plutonium contents ranging from 2 to 75 g in small cans up to 8 cm in diameter have been assayed. The number of U-loaded fuel plates in a fuel bundle has been determined in this way. The technique was used to see whether it was possible to detect a missing fuel plate (1 out of 19) or a substitute plate without U in a fuel bundle. The can assay system could be used for U, and the plate counter system could be used for Pu.

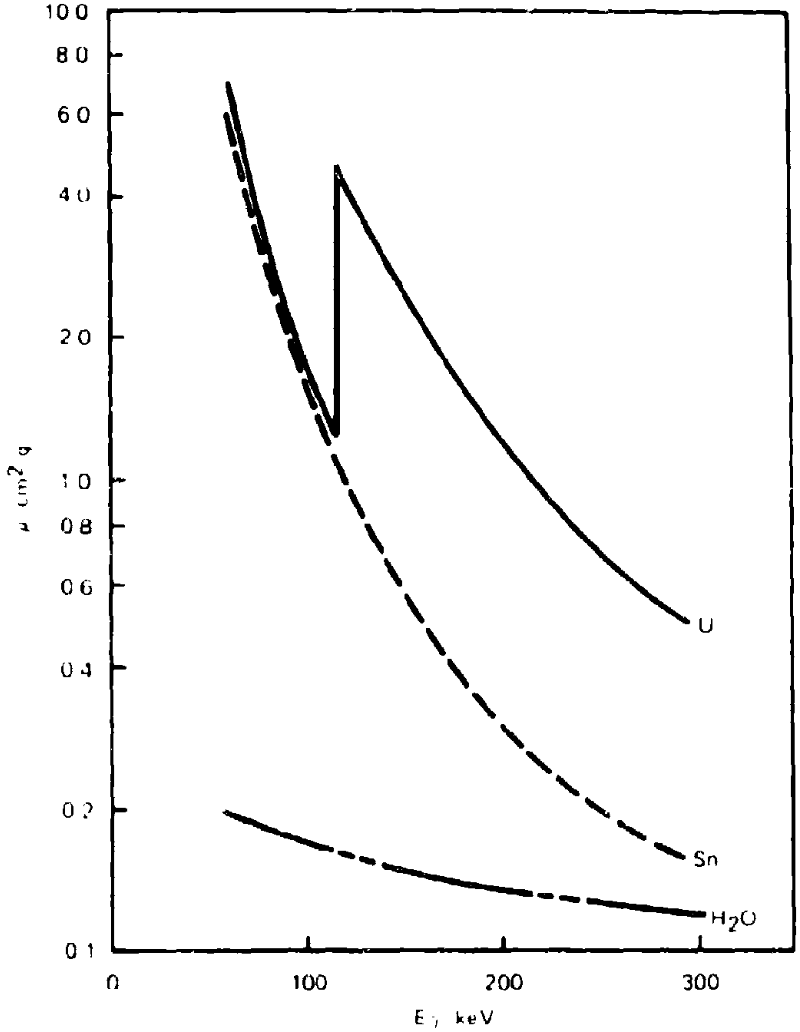

Figure 5.11 Mass attenuation coefficients as a function of gamma-ray energy for U, Sn, and H_2O. Note the *K* edge of U (from Ref. 26)

Table 5.7 Absorption edge energies[a]

Absorption Edge	Element	Edge Energy (keV)	$\Delta\mu_s$ (cm²/g)
L_{III}	U	17.17	54.60
	Pu	18.05	51.90
K	U	115.60	3.65
	Pu	121.79	3.39

[a] From Ref. 26.

Table 5.8 Sources for absorption-edge method: plutonium[a]

Source	E (keV)	$\Delta\mu_{Pu}$ (cm²/g)
^{75}Se (118 days)	121.1	2.12
	136.0	
^{75}Se	121.1	3.38
^{57}Co (270 days)	122.1	

[a] E_K = 121.8 keV; from Ref. 26.

Table 5.9 Sources for absorption-edge method: uranium[a]

Source	E (keV)	$\Delta\mu_U$ (cm²/g)
^{169}Yb (32 days)	109.9	2.20
	130.5	
^{169}Yb	109.8	2.70
^{57}Co	122.1	
^{182}Ta (115 days)	113.7	3.53
	116.4	

[a] E_K = 115.6 keV; from Ref. 26.

Summary of Performance

The performance of this technique is summarized in Table 5.10.

Equipment

Figure 5.8 shows a Pu solution assay system (Ref. 19). This system is also used for transmission-corrected assays. (See Section 5.2.1.3.) A

Table 5.10 Summary of performance: X-ray absorption-edge densitometry (*K*-edge)[a]

Sample Type	Concentration Range (g/L)	Sample Volume (mL)	Assay Time (min)	Performance (% RSD)		Ref.
				Random Error	Systematic Error	
U in nitric acid solution	50 to 500	20	17 to 34	0.4	([b])	27
Pu in nitric acid solution[c]	140 to 350	8	20 to [illegible]	0.1	0.4	28
Pu in incinerator ash	21.4, 51.4[d]	500	—	—	2	29

[a] All data from literature survey.
[b] Accuracy = 0.5 to 1.0 %
[c] Online system.
[d] Grams plutonium.

Ge(Li) detector is used for the K edge measurements. A Si(Li) X-ray detector is used with a similar system for the L edge measurements. Both systems require a shielded and collimated detector, liquid nitrogen cooling, preamplifier, amplifier, A/D converter, digital stabilizer, pileup rejector, multichannel analyzer or small computer, and power supplies.

For the K edge measurements, radioactive sources (see Tables 5.8 and 5.9) may be used. The sources would have to be replaced periodically because of radioactive decay. For the L edge measurements, a small filtered X-ray generator is required. Such an X-ray generator could also be used for the K edge measurements if a generator were purchased that could produce beams with photon energies up to 150 keV. For the L edge system with the X-ray generator the cost would be on the order of \$80,000 (Ref. 26). The K edge system would be \$20,000 or more, depending on the sophistication of the data handling system.

Sources of Error

At the low ranges of concentration there is little attenuation of the gamma rays. This leads to large uncertainties because the transmission ratio is near unity. At the high ranges of concentration the attenuation is large, and counting statistics with the sample may be poor because of a low count rate.

For the K edge measurements, the matrix sensitivity can be reduced by making E_u and E_l as close together as possible. When the ^{75}Se and ^{57}Co lines, 121.12 and 122.06 keV, respectively, are used (Table 5.8) the matrix sensitivity is small. For example, there is less than a 6% change in R for a 68-g/L Pu solution with the addition of Sn to a concentration of 1600 g/L. When the ^{75}Se lines at 121.12 and 136.0 keV are used, the assay would be in error by a factor of 3 for the same addition of Sn. A correction for the matrix interference can be made if the matrix has $Z > 50$ (Ref. 26).

The L edge measurements for U and Pu are subject to interferences by the K absorption edges of Y (17.04 keV) and Zr (18.00 keV), respectively. All other K edges present no problem. When these interferences occur, the L edge method cannot be used. In addition, calibration solutions may be subject to evaporation, which causes a slow increase of SNM concentration.

If different sample containers of nominally the same dimensions are assumed to have the same thickness when, in fact, there are small variations in critical dimensions, then there will be similar variations in predicted SNM content. A 1% variation in thickness will lead to a 1% variation in predicted SNM content ($\Delta \varrho_s/\varrho_s = \Delta x/x$).

Measurement Control Requirements

Calibration standards should be prepared to span the expected concentration range and should be similar in chemical composition, including impurities or other components. At least four different concentrations should be used. Solutions or metal foils can serve as working standards used to check system performance. Volumes of standard solutions should be monitored for possible evaporation. A working standard measurement should be made at least once a day if the system is being used. Additional checks should be made of the background, detector resolution, and peak position of the stabilization source. The consistency of dimension of different sample cells should be verified when results of the highest accuracy are required.

A calibration curve should be fitted using a least-squares technique. A fitting equation of the form

$$\varrho_s = a + b \ln R \qquad (5-16)$$

has been found to give satisfactory results. Figure 5.12 shows calibration curves used for *K* edge measurements of U solutions for various gamma-ray energy pairs (note the logarithmic ordinate). Calibration curves used for Pu show a similar behavior: as the difference in the energies of the pair of gamma rays bracketing the *K* edge increases, the response *R* is less sensitive to SNM concentration.

Data Analysis Requirements

The analysis of data collected for peak pair transmission measurements is similar to methods used for other Ge(Li) applications. Accurate determinations of net peak counts in multichannel spectra can be performed online by minicomputer programs or hard-wired options available with MCA systems. Close-lying doublets, such as may appear in the simultaneous measurement of the ^{75}Se (121-keV) and ^{57}Co (122-keV) peaks, will require special algorithms to determine the counts in each. The transformation of the transmission ratio into concentration can be accomplished using a previously prepared graph or table, or it can be part of a computer analysis.

Survey of Selected Literature

Uranium Nitrate Solutions (Ref. 27)

The material assayed consisted of U solutions with concentrations ranging from 50 to 500 g/L.

K edge densitometry was used to analyze 20-mL samples. The 110- and 130-keV gamma rays of a ^{169}Yb source were used for absorption-edge measurements with a Ge(Li) detector. Uranium metal foils were used to monitor instrument performance in later stages of the experiment. Freshly prepared solutions served as calibration standards in evaluating the accuracy of the measurement system.

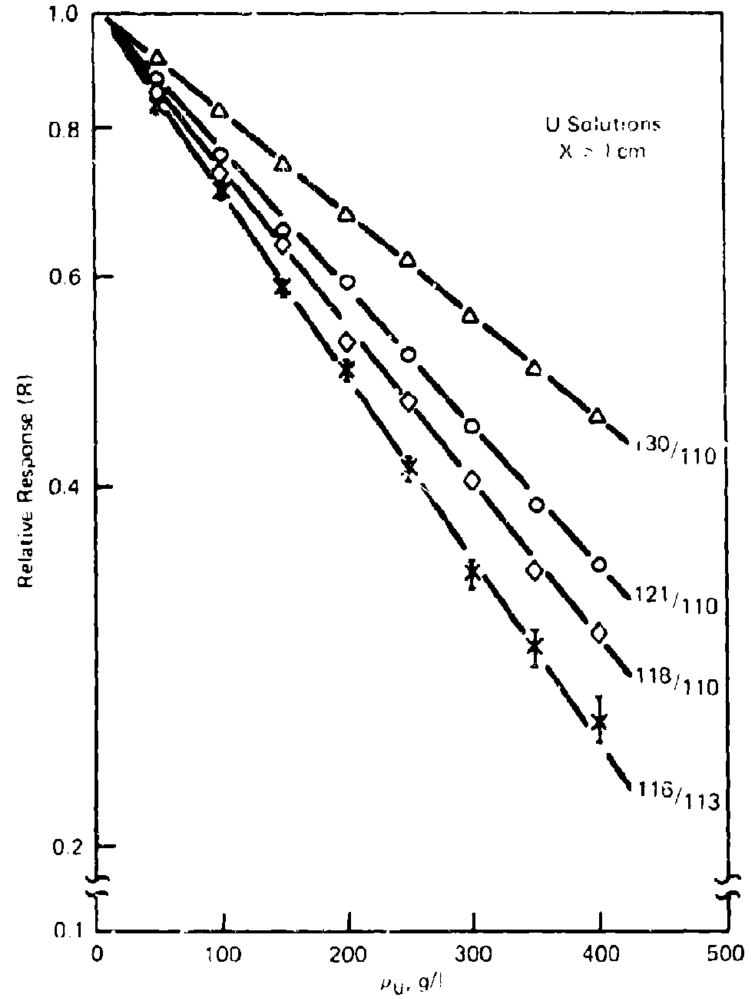

Figure 5.12 Calibration curves for *K* edge densitometry measurements for U solutions for several different gamma-ray pairs (from Ref. 26).

Repeated measurements of the metal foils showed a reproducibility of 0.4%. The system performed within its design parameters for which assay accuracies of 0.5 to 1.0% can be achieved for assay times of 1000 to 2000s. Monitoring instrument performance using standard solutions was unsatisfactory because of evaporation.

Plutonium Nitrate Solutions (Ref. 28)

The material assayed was Pu in 3*N* HNO_3 solutions with concentrations ranging from 140 to 350 g/L.

The concentrations of Pu solutions circulated through a 3.57 cm thick sample cell were measured using a *K* edge system that used ^{57}Co (1.6 mCi) and ^{75}Se (0.4 mCi) sources, a 2-cm^3 Ge(Li) detector, and a computer-based data acquisition system. Many replicate counts were taken to check the system stability. Calibration was performed with an in-house standard solution diluted to obtain 12 different concentrations. Counting times typically ranged from 20 to 40 min per sample.

The results from the calibration solutions were fitted by least-squares methods to the formula

$$\varrho_s = a + b \ln R \tag{5-17}$$

where *a* and *b* are calibration constants. The measured concentrations using the fitted curve agreed with the values from the chemical preparation within 0.44% RSD for recently separated Pu and 0.35% RSD for "aged" (simulated 15-yr-old) Pu. Repetitive counts indicated that a precision of 0.1% was obtainable.

Plutonium-Bearing Incinerator Ash (Ref. 29)

The material assayed was Pu ash in-house standards in 8.33-cm diameter cans containing 51.4 and 21.4 g of Pu.

The transmission ratio of gamma rays bracketing the Pu *K* edge was measured with an SGS system with a ^{75}Se source (E_γ = 121.1 and 136.0 keV). Scans were taken in 1.27 cm segments for a 10 cm height. The total mass was obtained from summing the results of the scans:

$$M_{Pu} = -\frac{h\pi d}{4\Delta\mu}\sum_i \ln R_i \tag{5-18}$$

where *h* is the scan height, *d* is the can diameter, $\Delta\mu$ is the difference in Pu mass absorption coefficients at the two gamma-ray energies, and R_i is the ratio of the 136- to 121-keV transmission.

The assay results, 21.4 ± 0.4 g and 51.4 ± 1.0 g, agreed well with the nominal values of 21.97 and 51.4 g, respectively.

5.2.1.7 Concentration Meter

Description of Method

For applications where the SNM concentration is uniform within an assay item, but where only gamma rays near the surface can escape, passive gamma-ray assay for SNM concentration is still possible under certain conditions. The conditions under which a gamma-ray system can be used as a "concentration meter" can be derived from Eq. 5–19. Using the 186-keV gamma ray from ^{235}U as an example, and for a sample thick enough to be considered "infinitely" thick, we have (Ref. 30)

$$CR = \frac{I\Gamma\varepsilon A F}{\mu_U} \qquad (5\text{–}19)$$

with

$$F = \left(1 + \frac{\mu_m \varrho_m}{\mu_U \varrho_U}\right)^{-1} \qquad (5\text{–}20)$$

where

CR = count rate for the 186-keV gamma ray, gamma ray/s
I = known ^{235}U enrichment
Γ = specific activity of the 186-keV gamma ray, gamma rays/s · g ^{235}U
ε = detection efficiency for the 186-keV gamma ray
A = effective area of sample viewed, cm^2
μ_U, μ_m = 186-keV mass absorption coefficients for U and matrix (cm^2/g), respectively
ϱ_U, ϱ_m = density of U and matrix in the solution (g/cm^3), respectively

For the concentration meter principle to be applicable, it is required that

$$\frac{\mu_m \varrho_m}{\mu_U \varrho_U} \gg 10 \qquad (5\text{–}21)$$

Equation 5–19 then simplifies to

$$CR \cong \frac{I\Gamma\varepsilon A \varrho_U}{\mu_m \varrho_m} \qquad)5\text{–}22)$$

$$\cong \frac{IK\varrho_U}{\varrho_m}$$

where K is a constant. The relative concentration in solution ϱ_U/ϱ_m is proportional to the 186-keV count rate, with an error of less than 10%. If Z_m

< 30 so that $\mu_m/\mu_U \approx 0.1$, then Eq. 5–21 is satisfied when $\varrho_m/\varrho_U > 100$. The mean free path for 186-keV gamma rays in low-Z material can be quite long, approximately 7 cm in water, so the amount of material needed to make an "infinitely" thick sample can be large. A sample thicker than 4.61 mean free paths can be considered "infinitely" thick to better than 1%.

Other applications of Eq. 5–19 can be used for thick samples. The most important of which is when $\mu_m\varrho_m/\mu_U\varrho_U < 0.1$. This application is used extensively for enrichment measurements and is discussed in Section 5.3.1.1.

Scope of Applications

The concentration meter can be used for any material containing uniformly distributed SNM where Eq. 5–21 is satisfied for the gamma ray of interest. Large volumes of contaminated matrix material or dilute solutions are examples of potential types of materials that could be assayed with this technique. Holdup measurements of contaminated Raschig rings in process tanks have been made. The technique can be used with any gamma ray, but generally only the 186-keV gamma rays from ^{235}U have been used.

Summary of Performance

Performance data not available for this method.

Equipment

The concentration meter requires a collimated detector [NaI or Ge(Li)], power supply, preamplifier, amplifier, and counting electronics. If there were no interfering gamma rays, a NaI detector would be adequate. A multichannel analyzer or small computer data acquisition system would simplify the peak area summation and background subtraction. The hardware for a system (NaI) without the multichannel analyzer would cost about $5000. Additional costs would be incurred for system design, testing, and calibration.

Major Sources of Error

The major sources of error arise from the need for an infinitely thick sample and for the satisfaction of the requirements of Eq. 5–21. Because this technique does not sample the entire volume, the SNM concentration must be homogeneous. The gamma-ray detector must be collimated to view only "thick" portions of the sample. If these requirements are not met, then large errors may result.

Measurement Control Requirements

The measurement control requirements for this type of system are similar to those of other NDA systems. Physical standards with approximately the same concentrations as the "unknowns" should be prepared, and a calibration factor should be determined relating detector response to SNM concentration. Detector/sample geometry and container-wall thicknesses should be kept constant when different containers are measured. Working standards and background should also be measured periodically.

Data Analysis Requirements

The computation of U concentration follows from Eq. 5–22:

$$\rho_U = \frac{\rho_m CR}{IK} \qquad (5-23)$$

If a calibration solution is used, then Eq. 5–23 simplifies to

$$\rho_U = K'CR \qquad (5-24)$$

where K' is a calibration factor.

Survey of Selected Literature

Uranium Deposits on Raschig Rings (Ref. 31)

The materials to be assayed consisted of low concentrations (<4 g/L) of HEU (93% ^{235}U) deposited onto Raschig rings from low-concentration solutions in cylindrical 440-L stainless-steel tanks approximately 30 in. in diameter and 36 in. high. The tanks contained 250 kg (110 L) of Raschig rings.

For this material $\mu_m \rho_m / \mu_U \rho_U \cong 46$, so Eq. 5–21 was satisfied. A mean free path in this material is 7.8 cm, so the sample was considered infinitely thick for a measurement taken along the tank radius. A portable NaI unit was used to measure the 186-keV gamma ray, and the data were corrected for wall attenuation. The system was calibrated by measuring the counting rate at the midplane of one of the tanks twice, first when filled with a U solution of known concentration (6.4 g/L), and then when empty.

In eight tanks the concentration varied considerably with height along the tank, with less U at the top than at the bottom. Total U was estimated by scanning an entire tank and integrating the results. Tank contents ranged from 26 to 599 g U. No values of precision or accuracy were given for the results.

5.2.1.8 Associated Radioactivity

Description of Method

In material containing ^{233}U, ^{235}U, or Pu, isotopes of other elements are often present in a fixed relation to these fissile isotopes. If a related isotope emits a characteristic gamma ray, either through its own decay or through a decay chain, then this gamma ray can be used for assay of a fissile isotope as well as for total SNM content. There are several different ways in which these relationships occur, and they are explained in the following paragraphs and in Section 5.2.1.10 dealing with isotopic correlation.

One of the problems of gamma-ray assay of ^{235}U is the variable amount of attenuation of the 186-keV ^{235}U gamma ray by matrix materials. Higher energy gamma rays are attenuated less, but no useful higher energy gamma rays come directly from ^{235}U. If the ^{235}U enrichment is known, then higher energy gamma rays associated with ^{238}U can be used for assay. This method uses the 767- and 1001-keV gamma rays that occur when ^{234m}Pa, a daughter product from the decay of ^{238}U, beta-decays to ^{234}U. The intensity of these gamma rays can be related directly to ^{238}U content. The sequence of decays resulting from the decay of ^{238}U is

$$^{238}\mathrm{U}(4.47 \times 10^{9}\ \mathrm{yr}) \xrightarrow{\alpha} {}^{234}\mathrm{Th}(24.1\ \mathrm{day}) \xrightarrow{\beta} {}^{234m}\mathrm{Pa}(1.17\ \mathrm{min}) \xrightarrow{\beta} {}^{234}\mathrm{U}$$

The amount of buildup of 24.1-day ^{234}Th in chemically separated U determines the intensity of the ^{234m}Pa gamma rays. Equilibrium is attained to within 1% 160 days after chemical separation of the Th from the U. At equilibrium the ^{234m}Pa gamma rays could be considered as originating directly from ^{238}U. If the sample is less than 160 days old and the time since separation is known, a simple decay correction can be made.

Gamma radiation from isotopes associated with ^{233}U can be used for assay purposes. The ^{232}U isotope is usually found in trace amounts in conjunction with ^{233}U. The presence of ^{232}U makes passive gamma-ray assay of ^{233}U difficult because the characteristic gamma rays coming directly from ^{233}U are masked by background from ^{232}U daughter gamma rays. If the ^{232}U/^{233}U isotopic ratio is known, however, it is possible to use the ^{232}U daughter gamma rays for assay under certain conditions (Refs. 32 and 33). The ^{232}U decay chain is shown in Figure 5.13. The most useful gamma ray in this chain results from the decay of ^{208}Tl(E_γ = 2.6 MeV). To relate the ^{208}Tl gamma-ray intensity to ^{232}U content, the chemical and temporal history of the sample must be known. The chemical history is required because chemical separations remove several or all the ^{232}U daughter products, changing the ^{208}Tl to ^{232}U relationship. The

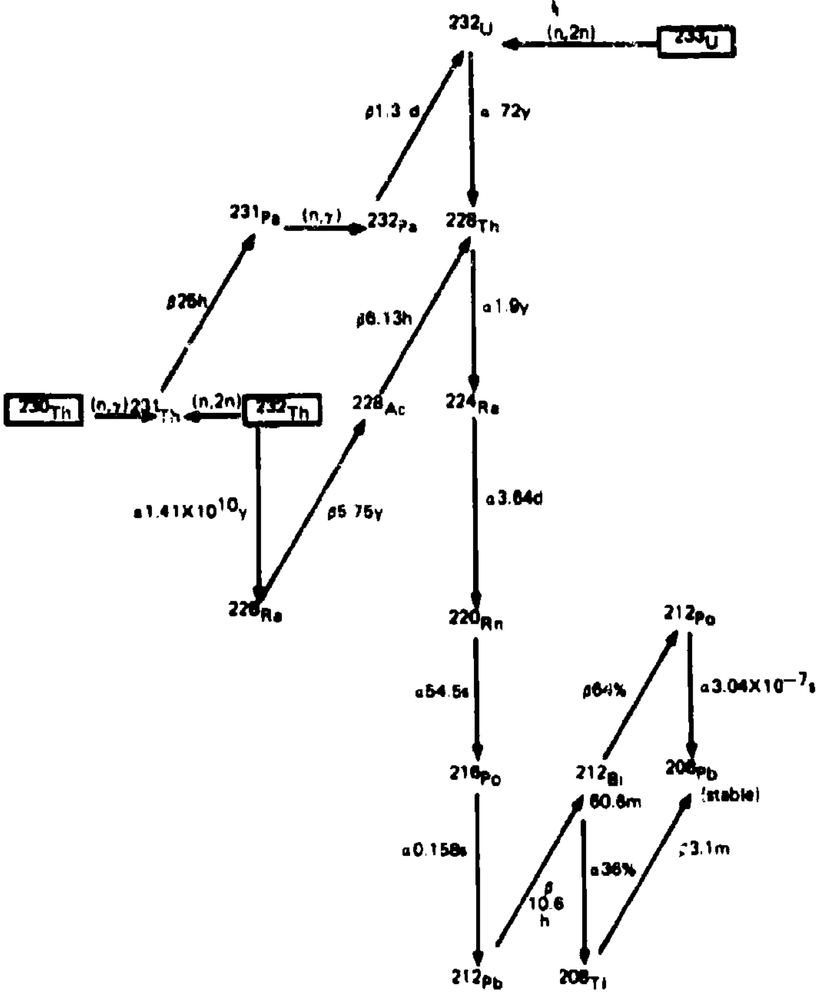

Figure 5.13 Production and decay chains of ^{232}U (from Ref. 32).

magnitude of the ^{208}Tl to ^{232}U conversion factor is dependent on the time elapsed since the chemical separation. The activity of ^{208}Tl is controlled by the half-life of ^{228}Th. The ^{208}Tl activity continues to increase relative to the initial amount of ^{232}U, reaching within 1% of equilibrium only after a period of about 14 yr.

Scope of Applications

This technique can be used to assay ^{238}U and ^{235}U in heterogeneous waste and in holdup measurements in plant process lines. Waste containing ^{233}U may also be assayed using ^{232}U daughter gamma rays.

Summary of Performance

A summary of the performance of this method is given in Table 5.11.

Equipment

For ^{233}U and ^{235}U assay by the associated radioactivity method, NaI detectors can be used, as the high-resolution capability of a Ge detector is not needed. The 766-keV and 1001-keV gamma rays from the ^{238}U daughter and the 2.6 MeV gamma ray from ^{208}Tl stand out in their respective spectra. Also, higher detection efficiencies are attainable with NaI because larger detectors can be made with NaI than with Ge.

An assay system consists of a Pb-shielded and collimated NaI scintillation crystal (the size depending on the application), photomultiplier, stable high-voltage supply, preamplifier, amplifier, two SCAs, two scalers, and a timer. A sample rotator could also be used. A portable electronics package that provides all these electronics except the preamplifier is available commercially. A multichannel analyzer is needed for the initial setup of the apparatus and for nonportable systems and could be used in lieu of the SCAs and scalers. The hardware for a complete portable system (detector plus electronics) is available commercially at a cost of $10,000 to $15,000. Additional costs would be incurred for system design, testing, and calibration.

Major Sources of Error

Although the penetrabilities of the ^{234m}Pa gamma rays are larger than that of the 186-keV gamma ray, a correction for matrix attenuation should be made, particularly for the large items typically assayed. A period of 160 days is required for the material to reach decay equilibrium, so the material must be properly aged for assay without the need for a decay correction.

A major source of error for ^{233}U assay arises in the determination of the proper conversion factor between the ^{208}Tl and ^{232}U activities. The material must be aged at least 16 days after solvent extraction or ion exchange to allow equilibrium with ^{228}Th and its daughter to be reestablished (Ref. 33). These chemical techniques remove different daughters in the decay from ^{232}U to ^{208}Tl and so change the decay chain for a short time until it is again dominated by ^{228}Th decay. The decay of ^{232}Th ($t_{1/2} \approx 1.41 \times 10^{10}$yr) also leads to ^{208}Tl through ^{228}Th and can cause an interference.

Table 5.11 Summary of performance: associated radioactivity[a]

SNM	Matrix and Container	Detectors	Calibrated Range (g)	Assay Time (min)	Performance	Ref.
LEU, less than 5% ^{235}U	Combustible; 3.5- by 4- by 4-ft wooden box	NaI, 5 by 5-in.	<750	4	([b])	34, 35
$^{233}UO_2$	Waste; 55-gal. drum	2 NaI, 3- by 3-in.	1 to 12.5	10	([c])	36

[a] All data from literature survey.

[b] "Limit of error" = 43%.

[c] 6% to 7% (95% confidence level).

The magnitude of this interference will depend on the ^{232}U content, age of the sample, and amount of Th present.

Measurement Control Requirements

For ^{235}U waste material measurements, representative calibration standards are required. More accurate results will be obtained if matrix inhomogeneities are minimized, and if wastes with different enrichments are segregated. The material to be assayed must be "aged" or its age must be known as discussed previously.

For holdup measurements (also discussed in Section 5.4), the system may be calibrated with known U sources. The measurements will be subject to corrections if the ^{234m}Pa has not reached equilibrium with the ^{238}U. Corrections for pipe-wall thicknesses need to be estimated. Self-attenuation in thick U deposits, such as those on the bottom of a pipe, must also be estimated if this is thought to be a problem.

Representative calibration standards are required for waste material measurements for ^{233}U assay and pose one additional complication relative to ^{238}U assay by associated radioactivity. This is the complication resulting from the long-term growth in ^{208}Tl activity. This complication can be surmounted by the use of archival samples, that is, samples having the same process history as the material being assayed in the waste. The conversion factor relating ^{208}Tl activity to ^{233}U content will be identical if the standard matches the "unknown" in both matrix properties and temporal history; however, an archival sample will be required for each historically different batch of waste.

After the initial calibration, a working standard with an activity and gamma rays similar to the unknowns should be measured at least twice per shift when the system is in use.

Data Analysis Requirements

By means of the activity of ^{238}U daughters, ^{235}U content may be determined by the following equation if a point calibration is assumed:

$$M_{235} = M_{238}\left(\frac{\mathrm{EN}}{100-\mathrm{EN}}\right) \qquad (5\text{-}25)$$

$$= \mathrm{CR}\,K\,\mathrm{CF}\left(\frac{\mathrm{EN}}{100-\mathrm{EN}}\right)$$

where

M_{235} = grams of ^{235}U
M_{238} = grams of ^{238}U
EN = known enrichment (weight percent of ^{235}U)
CR = net count rate for 767- and/or 1001-keV gamma ray for sample
K = empirically determined calibration factor [g(^{238}U)/(count/s)] for the 767- and/or 1001-keV gamma ray
CF = correction factor for attenuation in the sample estimated from sample composition and mass or by a separate transmission measurement

Details and an error analysis of this calculation are given (for waste assay only) in Reference 34.

The ^{233}U content of a sample is determined, using associated radiation from ^{232}U daughters and assuming a point calibration, by the equation

$$M_{233} = \mathrm{CR}\,K\,\mathrm{CF} \qquad (5\text{–}26)$$

where

M_{233} = grams of ^{233}U
CR = net count rate of sample from a ^{232}U daughter
K = calibration factor [g(^{233}U)/(count/s)] for an archival standard in which the count rate is for a ^{232}U daughter: viz ^{208}Tl.
CF = correction factor for the attenuation in the sample estimated from sample composition and mass or by a separate transmission measurement

For the above measurements the calibration source and assayed items should be counted in similar, if not identical, geometries. Further details and an error analysis for the calculation of ^{233}U in waste are given in Reference 36.

Survey of Selected Literature

Combustible/Noncombustible Waste Standards (Refs. 34 and 35)

The material assayed was U (0.22 to 3.3 weight percent ^{235}U) distributed in combustible and noncombustible waste in wooden crates with dimensions of 107 by 122 by 122 cm and total container weights ranging up to 2350 kg.

An assay system consisting of a 5-in. diameter by 5-in. thick NaI detector with lead shield and collimator 2 in. thick was used for the measurement. A similar system (nicknamed "elephant gun") is shown in Figure 5.14. Calibration standards were made by filling five cans with known amounts of UO_2 powder (150 g of 3.02% enriched U per can) in a paper matrix. The cans were placed in different locations in a waste box, and an average response was determined. An attenuation correction factor based on gross waste-container weight was calculated and tested against the attenuation measured with a ^{137}Cs source. Good agreement was obtained. For the assay of the samples, each box was measured twice, once each on opposite sides for 2 min, and the results were averaged. An average facility enrichment was calculated based on known enrichments of the U processed in the facility so the assayed value of ^{238}U could be related to grams of ^{235}U.

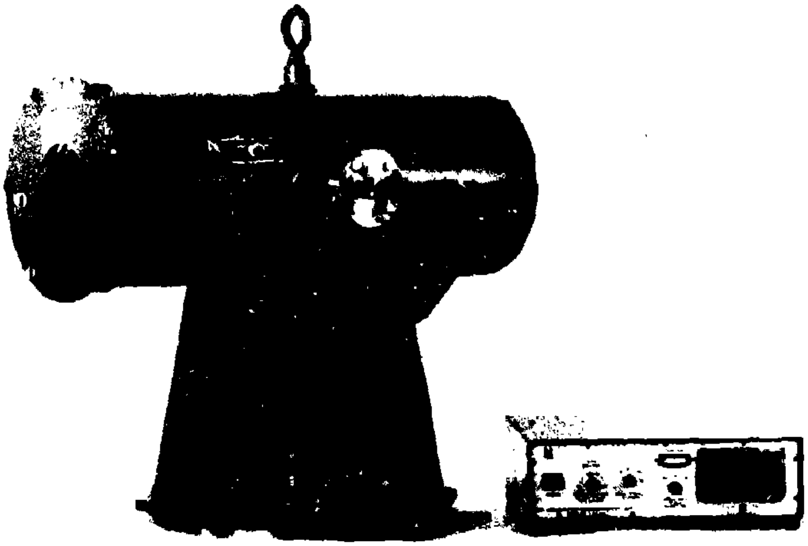

Figure 5.14 An "elephant gun" NaI detector and portable electronics package. (Photograph courtesy of National Nuclear Corporation.)

The total relative errors from a "limit-of-error" analysis were calculated to be 16% for ^{238}U and 43% for ^{235}U for the assay of a box of waste. The system is capable of detecting 30 g of ^{238}U at sea level in a 5-min count. The sensitivity would be less at higher altitudes because of increased cosmic ray background. The system has been used routinely for accountability measurements for more than 5 yr at a LEU fuel-fabrication facility.

U Waste Standards (Ref. 36)

The material assayed was ^{233}U as UO_2 with less than 10 ppm ^{232}U in waste and in five 55-gal. drums with measured ^{233}U amounts ranging from 17 to 32 g.

Two 3-in. diameter by 3-in. high NaI detectors viewed the upper and lower halves of a rotating drum. The 1.4- to 2.8-MeV region of the gamma-ray spectra encompassing the ^{208}Tl gamma-ray peaks (full energy, single and double escape) was integrated. Uranium-233 content was estimated by comparison with an archival standard. Transmission measurements were also taken to correct for matrix attenuation.

The assay of the five drums yielded values that had 95% confidence limits ranging from 6% to 7%. These values include the uncertainties from SNM location in the container, counting statistics, and the weights of the standard and samples.

5.2.1.9 Passive X-Ray Assay

Description of Method

Because X-rays are emitted by U following the alpha decay of Pu to U, these X-rays can be used for the assay of Pu under certain conditions. The conditions are that the matrix material have $Z \leq 8$ and low density $\leq 0.2\ g/cm^3$ and that the Pu be uniformly dispersed as small particles throughout the matrix. The first two conditions allow the X-rays to traverse the matrix material without severe attenuation. The last condition limits the effect of self-attenuation in the SNM. Only *L* X-rays are used (13 to 30 keV in energy) because they are at least 500 times more intense than *K* X-rays. *L* X-ray specific activities for the Pu isotopes and ^{241}Am (Ref. 37) are as follows:

^{238}Pu	7.4×10^{10} X-rays/s·g
^{239}Pu	9.7×10^{7} X-rays/s·g
^{240}Pu	8.8×10^{8} X-rays/s·g
^{242}Pu	1.4×10^{7} X-rays/s·g
^{241}Am	4.6×10^{10} X-rays/s·g

The X-ray assay technique is used for small amounts of SNM (in waste material), because the X-ray specific activity for the Pu isotopes is hundreds to thousands of times larger than that of any of the major gamma rays. Where larger amounts of SNM are present, the higher energy gamma rays can be used for an assay less affected by attenuation in the sample.

Scope of Applications

The principal application of this technique is the assay of low-density, low-*Z*, transuranic, contaminated waste at levels of 10 nCi/g (or less).

The technique is used primarily in waste management. It is used to decide whether discarded material can be categorized as low-level waste. The cutoff level of 10 nCi/g corresponds to 560 μg of ^{239}Pu (6% ^{240}Pu) in 4 kg of waste. The assay value can also be used for accountability purposes; however, the amount of material measured will be negligible compared with throughput or inventory quantities normally encountered in production facilities.

This technique is not used for ^{235}U assay because the *L* X-ray specific activity resulting from ^{235}U decay is less than that for the 186-keV gamma ray. Also this gamma ray assay is less sensitive to matrix interference than the lower energy *L* X-rays, and thus is more suitable for assay.

Summary of Performance

A summary of the performance of this method is given in Table 5.12.

Equipment

Because small quantities of Pu are to be detected, a large-area detector is required. NaI scintillators 12.7 cm in diameter and as thin as 0.16 cm with thin (0.25 mm) Be windows have been used for X-ray assay. Using thin NaI crystals enhances detector sensitivity in that the detectors are thin enough to completely absorb the low-energy *L* X-rays, but the probability of interaction and, hence, of the Compton background from higher energy gamma rays from fission-product contamination and SNM is minimized. The presence of fission-product peaks in the *L* X-ray region requires the superior resolution of Ge detectors for assay of Pu and Am.

The equipment needed is a shielded and collimated NaI detector, photomultiplier with base circuit, power supply, preamplifier, amplifier, and SCAs or a multichannel analyzer or a small computer. To assay boxes, rotation and translation are desired to reduce geometric uncertainties.

The hardware cost of a system with a simple multichannel analyzer and no box scanning would be about $20,000. Adding box scanning, automatic weighing, and computer control would increase the cost to the $40,000 to $70,000 range. Additional costs would be incurred for testing and calibration.

Major Sources of Error

Self-attenuation in the SNM of the 17-keV *L* X-ray can be a major source of error. Calculations show that self-attenuation of these X-rays can reduce the intensity by 50% for a Pu sphere as small as 20 μm in diameter (Ref. 38). This effect, as well as matrix attenuation, can be compensated for by calibration with representative standards, but excessive self-attenuation will still occur if lumps of SNM are present. Another

Table 5.12 Summary of performance: passive X-ray assay[a]

Sample Type (mass)	Isotopic Composition	SNM Content (nCi/g)	Sample Size (L)	Counting Time (s)	Performance[b] Random Error (%)
Pu in combustible waste:	94% ^{239}Pu,	3.9	60	200	10
7.0 kg	6% ^{240}Pu				
5.6 kg	94% ^{239}Pu,	14		500	11
	6% ^{240}Pu				

[a] All data from Ref. 37; multienergy gamma assay system (MEGAS).

[b] Accuracy $\leq$ 50%.

source of error is the variation in response because of localization of SNM in extreme locations of the box.

A major interference is the contribution to the *L* X-ray peak by X-rays from ^{241}Am decay. A correction can be made for this interference based on the measured intensity of the 60-keV gamma ray from ^{241}Am. Fission-product X-rays from ^{95}Zr and ^{106}Rh will also interfere with the *L* X-rays. A check of the region above 500 keV can be used to determine whether fission products are present. When fission products are present, either the assay can be terminated because of the interference with the X-ray region, or a correction can be made for the interference. In one case (Ref. 37), the interference decreased the assay sensitivity by about a factor of 10.

Measurement Control Requirements

Representative calibration standards and a working standard (for example, a 0.7-mg ^{239}Pu source) are required. To correct for the contribution of ^{241}Am *L* X-rays to the Pu X-ray peak, an ^{241}Am standard is also needed. The calibration standards must duplicate the sample matrix and SNM particle size. The system should be checked for drift and changes in background at least once a day. A calibration curve should be used for the determination of absolute amounts of Pu, assuming a given isotopic composition of Pu.

Waste sorting must be performed before the assay to ensure that only low-density material, such as paper, is being measured. Pieces of glass and metal must be removed prior to assay.

Data Analysis Requirements

The amount of Pu in the sample is calculated using the following equation to determine *N*, the net number of counts in the L X-ray peak from Pu:

$$N = C_X - C_{60}F \qquad (5\text{–}27)$$

where

C_X = net counts per second for the *L* X-ray peak
C_{60} = net counts per second for the ^{241}Am 60 keV gamma-ray peak
F = ^{241}Am (X-ray)/^{241}Am (60-keV gamma ray) ratio measured for the ^{241}Am standard

Once *N* is determined, the amount of Pu is determined from a calibration curve. For waste management purposes, quantities are usually expressed as nanocuries per gram of sample by converting grams of plutonium to nanocuries (assuming a given Pu isotopic composition) and dividing by the total mass of the sample.

Survey of Selected Literature

Plutonium in Low-Density Waste (Refs. 37 and 39)

The material assayed consisted of Pu (94% ^{239}Pu, 6% ^{240}Pu) in 60-L cardboard boxes containing low-density wastes (such as paper and plastic) with measured Pu content ranging from 0.04 to 400 mg.

Two different systems were used to assay the material. The first (pancake counter, Fig. 5.15) used a 12.7-cm diameter and 0.16-cm thick NaI(Tl) crystal with a 0.025-cm Be window. This detector was of the Field Instrument for Detection of Low-Energy Radiation (FIDLER) design (Ref. 40). The detector was placed about 10 cm from the samples, which could be up to 46 cm in diameter and 20 cm high. The electronics used with this detector included an amplifier, two SCAs (set for the 17- and 60-keV regions), two scalers, and a timer.

The second system (Fig. 5.16) used a shielded 12.7-cm diameter, 5.0-cm thick NaI scintillator with a 0.025-cm Be window. This system is the

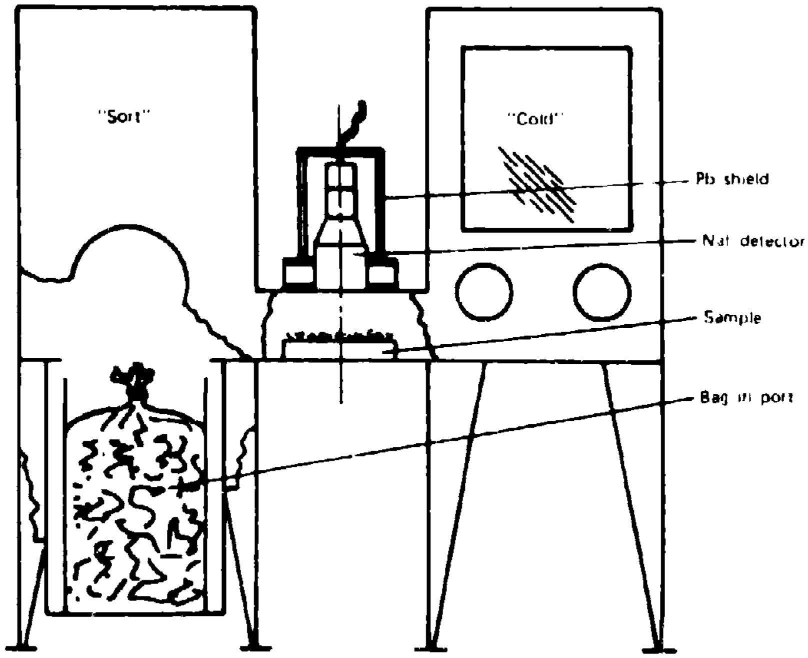

Figure 5.15 Schematic of waste sorting line and Pancake Counter. (Figure courtesy of Los Alamos National Laboratory.)

Figure 5.16 System components for a Multienergy Gamma-ray Assay System (MEGAS). The detector is shielded by lead blocks (located upper right). (Photograph courtesy of Los Alamos National Laboratory.)

Multienergy Gamma Assay System (MEGAS), which uses X-ray assay for Pu determination and can also measure Pu content based on higher energy gamma rays. Sample rotation and translation is used during the assay. The MEGAS is a computer-based system that uses the scintillator detector to investigate several areas of the X- and gamma-ray spectrum to assay for Pu, Am, U, and the presence of fission products. The U assay is based on the 186-keV gamma ray from ^{235}U. Another window is set to measure the ^{137}Cs fission-product gamma rays. The ^{241}Am content is determined from the 60-keV gamma rays. For samples containing Pu yielding an activity greater than 35 nCi/g, the 400-keV region of the gamma-ray spectrum is used for Pu assay. For samples with activities below 35 nCi/g, the *L* X-rays from Pu decay are used for the assay after a correction for the ^{241}Am contribution.

Cardboard boxes of waste were assayed with MEGAS. The contents of these boxes were removed, sorted, and then repackaged into 10 to 20 discrete packets for analysis with the pancake counter.

Samples with Pu contents ranging from 0.2 to 1 mg were measured with both the pancake counter (10-s counting time per packet) and the MEGAS (500-s counting time per box). The results agreed within the stated uncertainties. For example, for one box assayed with the MEGAS and pancake counter, activities of 3.0 ± 1.5 and 6.3 ± 3.2 nCi/g, respectively, were obtained. The measurement accuracies of both the pancake counter and the MEGAS are limited to 50% because of spatial variations in the SNM locations. For repeated counts taken over a period of several weeks of an in-house standard of 4 nCi/g, the MEGAS yielded a result of 3.9 nCi/g with a 10% precision. The pancake counter yielded a result with better precision (less than 10% standard deviation).

Of primary importance for these instruments are their sensitivity levels, because these instruments are used to decide whether material can be discarded for burial. Using the *L* X-rays, the MEGAS has a detectability limit for Pu (6% ^{240}Pu) ranging from 0.13 to 0.04 nCi/g for 100- and 1000-s counts, respectively, for 4000 g of waste in a 60-L paper box. These limits are equivalent to 7.0 μg and 2.2 μg of Pu per box. A limit for the pancake counter was 1.1 nCi/g or 6 μg for a 10-s count of Pu in 390 g of waste in a plastic bag. Detectability is defined here as the amount of material that would give a response three times the standard deviation of the background.

The MEGAS has been used routinely for measurement of contaminated waste with a reported throughput per month of 155 60-L boxes of waste containing a total mass of approximately 770 kg. The counting time used (200 s) was such that 10 times that throughput could be accommodated. Modifications and improvements to the MEGAS are under development and are described in Reference 39.

5.2.1.10 Isotopic Correlation Measurements

Description of Method

An isotopic correlation is a relation, expressed either algebraically or graphically, between the measured amounts of certain fission products or heavy element isotopes present in irradiated nuclear fuel and some other quantity or parameter of interest, such as total Pu content, Pu/U ratio, burnup, or fuel cooling time. By using a correlation one can provide an independent verification of the direct measurement of these quantities. NDA techniques are useful here because they can be used to measure the correlated isotope(s) and quantities of interest with minimal or no processing of highly radioactive fuel materials. This is significantly simpler than chemical techniques. This field is under active development, especially in Europe. In this subsection, the use of passive gamma-ray NDA for isotopic correlation measurements will be discussed.

Correlations have been established with indicators for isotopes of the heavy elements (such as ^{235}U, ^{239}Pu, and ^{242}Cm), isotopes of stable fission products, and isotopes of radioactive fission products. Passive gamma-ray assay can be applied only to the last category, fission products. Interference from the fission-product gamma rays makes direct gamma-ray assay of the heavy isotopes impossible. Table 5.13 lists some of the isotopes that can be used as indicators of Pu/U ratios or burnup.

To establish a correlation, initially both the indicator (for example, the ^{134}Cs/^{137}Cs ratio) and the quantity of interest (for example, the Pu/U ratio) must be determined independently. The quantity of interest may be determined either through extensive reactor calculations or by analytical techniques used on actual fuel elements. Reactor calculations can also reveal which quantities could be the most useful indicators. Many indicators have been investigated as functions of reactor type and power generation history. An example of an isotopic correlation is

$$y = a + bx \qquad (5\text{-}28)$$

where

y = predicted Pu/U mass ratio
x = ^{134}Cs/^{137}Cs mass ratio
a,b = constants previously determined through least-squares fitting (Ref. 42).

Correlations established through analytical and gamma-ray spectrometric techniques apply only to a particular type of reactor and a particular type of fuel. A major effort in the study of isotopic correlations is the establishment of data bases for various reactors that include information such as U, Pu, and fission product abundances, operating history, and initial U enrichment. Such data are analyzed to establish correlations.

The degree of specificity required can be seen in Table 5.14, which lists the performance of indicator ^{134}Cs/^{137}Cs for various reactor types. Absolute activities of certain fission products may also be used as indicators.

A large body of information is available on the development of NDA techniques and the use of analytical techniques for isotopic correlations. Summary papers have been published (see Refs. 41 through 44) with extensive bibliographies.

Scope of Applications

The method of isotopic correlations by passive gamma-ray assay has had its most promising application with PWR spent fuel. Simple correlations have not been established for BWR fuel. In cases where the correlation has been established, the estimation of the Pu/U ratio obtained through the use of correlated isotopes could be used to verify chemical measurements of the Pu content of irradiated fuel that are made at a reprocessing plant. Similarly, the remaining ^{235}U content of irradiated fuel can be estimated through the measurement of isotopes correlated with burnup.

Table 5.13 Radioactive fission isotopes for burnup monitoring[a]

Nuclide	Half-life	Thermal Neutron Fission Yield (%)		Principal Gamma Rays	
		^{235}U	^{239}Pu	Energy (keV)	Branching (%)
^{95}Zr	65.5d	6.50	5.01	724.18	44.4
				756.72	54.6
$^{106}Ru-^{106}Rh$	369d	0.39	4.48	511.85	20.6
				621.87	9.8
				1050.39	1.5
				1128.07	0.4
^{134}Cs	2.06 y	6.75[b]	7.42[b]	569.35	15.4
				604.73	97.6
				795.84	85.4
				801.94	8.7
				1365.0	3.3
^{137}Cs	30.12 y	6.36	6.65	661.64	85.0
$^{144}Ce-^{144}Pr$	284.4 d	5.39	3.80	696.49	1.51
				1489.1	0.29
				2185.7	0.74
^{154}Eu	8.6 y	0.164[c]	0.285[c]	591.78	4.9
				723.31	19.7
				873.25	11.7
				996.37	10.1
				1274.50	34.7

[a] From Ref. 41.

[b] Yield of ^{133}Cs.

[c] Yield of ^{153}Eu.

Table 5.14 Standard errors of burnup or Pu/U ratio from nondestructive measurement of ^{134}Cs/^{137}Cs activity ratio[a]

Reactor Type Fuel Cycle	Correlation Between ^{134}Cs and ^{137}Cs	Burnup Range (MWD/MTU)	Source Configuration	Standard Error[b] (%)
Sena (PWR), 1st cycle	^{137}Cs	12,600 to 13,150	Rod	3
Sena (PWR), 2d cycle	^{137}Cs	18,600 to 20,300	Rod	13[c]
Sena (PWR), 1st cycle	Burnup	12,600 to 13,150	Assembly midpoint	3.7
Trino (PWR), 2d cycle	Burnup Pu/U	18,500 to 22,500	Assembly[d]	1.1 1.2
Trino (PWR), 3d cycle	Pu/U	19,700 to 28,700	Assembly[d]	2.1
Dodewaard (BWR)	Burnup	6000 to 17,000	Rod	8.5
JDPR-I (BWR)	Burnup	1900 to 7000	Rod	(e)
Garigliano (BWR)	Pu/U	7000 to 18,500	Assembly[d]	(f)

Note—See footnote at end of table.

Table 5.14 Standard errors of burnup or Pu/U ratio from nondestructive measurement of $^{134}Cs/^{137}Cs$ activity ratio[a] (Cont'd)

Reactor Type Fuel Cycle	Correlation Between ^{134}Cs and ^{137}Cs	Burnup Range (MWD/MTU)	Source Configuration	Standard Error[b] (%)
Bohunice (CANDU-Type)	Burnup	1800 to 8000	Bundle	5 to 7.6
NPD (CANDU)	Burnup	6000 to 10,150	Bundle midpoint	1 to 7.3
PRTR[g]	Burnup	9000 to 14,000	Rod	2.0
	Pu/U			1.3

BWR = boiling water reactor; PWR = pressurized water reactor.

[a] From Ref. 41.

[b] The standard error is calculated, whenever possible, by fitting the data to a linear regression equation $Y = a + bx$. The standard error about the regression is

$$\sqrt{\sum_{i=1}^{n} (y_i - Y_i)^2/(n-2)}$$

where y = experimental values, Y = values predicted from the regression line, and n = number of observations.

[c] Systematic error. This deviation is attributed to the lack of power history correction.

[d] Assemblies were assayed at eight to nine levels and four corners, and the ^{134}Cs and ^{137}Cs activity ratios were summed.

[e] Upper and lower segments differ by 20%.

[f] No correlation; if power history correction is made, the standard error is 3.9%.

[g] Plutonium recycle test reactor with natural uranium oxide fuel.

Summary of Performance

A performance summary is given in Table 5.15.

Equipment

For passive gamma-ray isotopic correlation measurements a detector, preamplifier, amplifier, multichannel analyzer or small computer, and power supplies are needed. A Ge detector is needed in most cases to resolve the gamma rays of interest; however, NaI detectors have been used to measure the well-separated ^{144}Pr (2186 keV) gamma ray from leached hulls. Gamma-ray shielding may be needed to reduce the interference from other nearby fuel assemblies or SNM solutions. For passive measurements of fuel bundles under water, the detector must be encased in a water-tight and shielded container, positioned near the bundle. Alternatively, an air-filled collimator that reaches from the fuel to the detector may be used to reduce the gamma-ray attenuation in the water shield. Shielding or use of a small aperture (for example, a 5-cm diameter pipe 6 to 9 m long) is required to reduce the gamma-ray intensity at the detector. Provision for measurements made through a hole bored in the side of the cooling pond might be considered in its design.

The hardware for a gamma-ray assay system would cost from $20,000 to $30,000 or more depending on the sophistication of the data acquisition and analysis system desired. Additional cost would be incurred for system design, testing, and calibration. A leached hull monitor system using a NaI detector is estimated to cost $100,000.

Major Sources of Error

One significant source of uncertainty in an isotopic correlation technique is in the determination of the isotopic correlation itself. The correlation used must be applicable to the particular reactor type of interest. The correlation indicator may be dependent upon the reactor type, the operating history including the reactor power levels, the use and positions of control rods during operation, and the cooling time. For fuel assemblies, the burnup can vary up to 40% with vertical and radial position. These factors, along with the experimental uncertainties of the analytical measurements, lead to uncertainties in the correlation equation.

The power histories of assemblies are particularly important when ^{134}Cs data taken from different loading cycles are compared. The form of the correlation constants will vary because of the different formation rates of ^{134}Cs and its subsequent decay. To adjust for this effect, the power history of the reactor must be known. The longer lived ^{154}Eu is less sensitive to the power history, and the ^{154}Eu/^{137}Cs ratio is preferable as an indicator. Because the fission yield is small, however, one must allow the

Table 5.15 Summary of performance of passive gamma-ray techniques on spent fuel for burnup (HEU) or Pu/U content[a]

	Correlation	Material	Gamma-Ray Ratio Reproducibility (% RSD)	Correlation Calibration Error (% RSD)	Ref.
^{134}Cs/^{137}Cs	Pu/U	Dissolved fuel	0.5	1.2	45, 46
	Pu/U[b]	PWR assemblies	0.5 to 0.8	1.3, 2	
	Burnup	MTR assemblies	—	8[c]	44
^{154}Eu/^{137}Cs	Pu/U	Dissolved fuel	1	2	45, 46
	Pu/U[b]	PWR assemblies	5.2, 6.8	5.6, 8.7	
^{144}Pr	U	Leached hulls	([d])		47, 48

MTR = materials testing reactor.

[a] All data from literature survey.

[b] Calculated ratio.

[c] 95% confidence level.

[d] Sensitivity is equal to 1 g U per metric ton hulls.

fuel to cool for a longer period before the ^{154}Eu gamma-ray peak is measurable (Ref. 43).

Attenuation of gamma rays by the fuel bundle requires careful attenuation corrections and detector collimator positioning. Where the indicator is based on a ratio of two isotopes, different radial migration rates may occur because of the different methods of formation of the isotopes, and different attenuations may result (Ref. 43).

Measurement Control Requirements

Chemical measurements used to establish the correlation curve should be traceable and accurate; any systematic error in the chemical assay will contribute to the systematic error of the NDA estimate. The power history and cooling time of the irradiated fuel must be known to correct for decay. The form of the calibration curve is determined from the isotopic correlation and is not necessarily linear.

When the absolute activity of an indicator is required, the detector efficiency for the particular gamma-ray energy must be known. The detector efficiency depends on the measurement geometry as defined by the collimator and the intrinsic efficiency of the detector. Calibrated sources used for determination of this efficiency should be measured at the same geometry as the assay, and this geometry should subsequently be maintained. Dead-time corrections, using pulsers, are required for the irradiated fuel assays because the count rates are usually high. Ratio measurements (for example, ^{134}Cs/^{137}Cs) are independent of the need for absolute calibration.

For fuel assemblies in a cooling pond, background measurements can be made while another fuel assembly is being moved into the measurement position. Directional collimators are required when assemblies cannot be moved out of the way.

Data Analysis Requirements

An example of an isotopic correlation relationship was given in Eq. 5–28. The ^{134}Cs/^{137}Cs mass ratio is determined from the areas under gamma-ray peaks for ^{134}Cs and ^{137}Cs. For both ratio and absolute measurements, the integrated counts must be corrected for detector efficiency differences, energy dependent attenuation in the sample, and background. The data may be accumulated with a multichannel analyzer or small computer. Once the peak integrals are obtained, only simple calculations are needed, but a computer is helpful for the statistical analysis of the data and curve fitting.

The total Pu content of the measured material may then be determined, using the Pu/U ratio calculated from an isotopic correlation (IC), by

$$Pu = (Pu/U)_{IC} \times U' \qquad (5-29)$$

where U′ is the initial U content minus burnup.

The initial U loading is well known (systematic error = 0.05%) from fuel fabricator data, and the amount of ^{235}U used up (burnup) can be calculated within ±5%. Because for commercial power reactors this corresponds to only 2% to 5% of the total U, the total U remaining (initial U minus burnup) can be calculated quite accurately (Ref. 49). The standard error of the predicted $(Pu/U)_{IC}$ ratio can be estimated by measuring the deviations about the regression line. The magnitudes of some of these standards errors are listed in Table 5.14.

Survey of Selected Literature

Burnup of MTR Fuel Elements (Ref. 50)

The material assayed was 10 MTR type fuel elements, 108 by 7.6 by 7.6 cm, containing 18 curved plates 1.53 mm thick. Each plate holds U-Al alloy fuel. 0.31 mm thick, sandwiched between two 0.51-mm sheets of Al. The alloy mixture is 93% Al and 7% HEU (93% ^{235}U). Each fuel element was in the core approximately 3 yr in the Omega West Reactor operated at a maximum power of 8 MW for one shift per day, 5 days per week. Cooling times were 341 to 1445 days.

A Pb-shielded Ge(Li) detector and counting electronics, including a multichannel analyzer, were used. For the burnup measurements the detector viewed the entire length of the fuel element through an air-filled aluminum collimator. The experimental arrangement is shown in Figure 5.17. The collimator was used as shown for profile measurements. The $^{134}Cs/^{137}Cs$ ratio was measured using the 605- and 662 keV lines of ^{134}Cs and ^{137}Cs, respectively. Counting times of 15 min were used and background was measured while fuel elements were moved from storage to the pool. Each fuel element was measured once. No calibration standards were required for the ratio measurements, and only relative data were obtained for the profile measurements. The data were not corrected for differential attenuation in the fuel.

The measured ratios were compared to declared burnup values, and the following equation was determined from a least-squares fit to the data:

$$y = 19.5 + 46.6x \qquad (5-30)$$

where y is the burnup and x is the $^{134}Cs/^{137}Cs$ ratio. At $x = 1, y = 66 \pm 5$ g (95% confidence level).

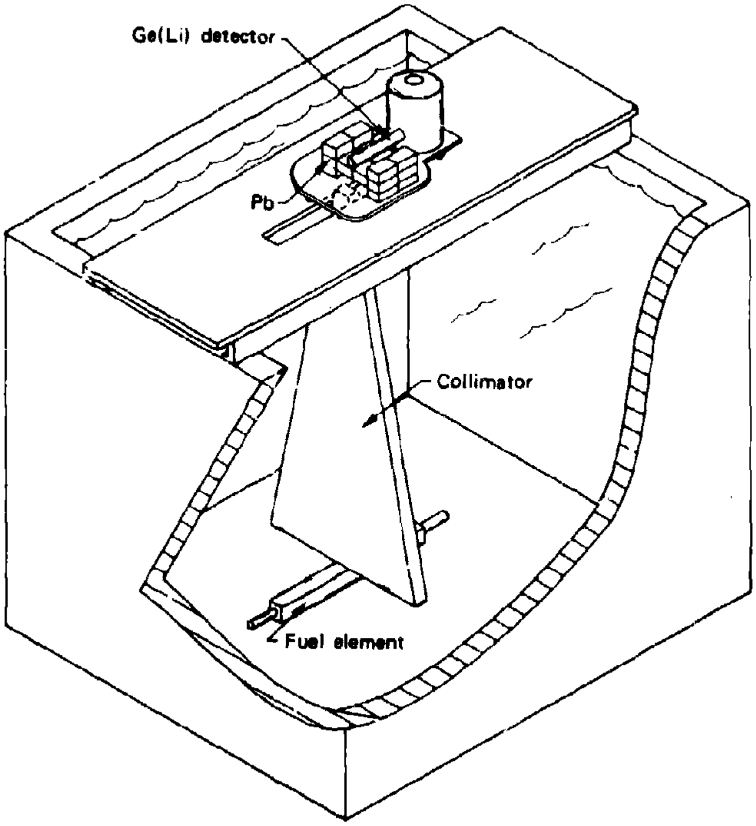

Figure 5.17 Apparatus for $^{134}Cs/^{137}Cs$ isotopic correlation measurements. The collimator was rotated 90° during the burnup measurements to view the entire fuel element.

Uranium in Leached Hulls (Refs. 47 and 48)

The material assayed was U in leached hulls from irradiated fuel elements. The hulls are contained in a basket 91 cm in diameter and 213 cm high. The basket can hold the hulls from 1 metric ton of fuel.

A leached-hull monitor for a reprocessing plant was designed to assay the amount of U remaining undissolved in leached fuel-element hulls. The determination is based on the measurement of the intensity of the ^{144}Pr 1489- and 2186-keV gamma rays. Praseodymium-144 is the daughter of ^{144}Ce decay, and the ^{144}Ce occurs as a fission product. The principal assumption of this method is that ^{144}Ce and U will occur together in a fixed proportion. The calibration of the system would be through destructive analysis of a batch of leached hulls.

The leached-hull monitor consists of a 5-in. diameter by 5-in. thick NaI scintillator, associated electronics including a fast/slow background suppression system, a Pb filter, and a Pb collimator. The large scintillator is needed for efficient detection of the ^{144}Pr gamma rays. The fast/slow system reduces interference from other gamma rays, especially ^{60}Co. The Pb filter reduces the lower energy gamma-ray background, and the collimator allows the detector to view only the leached-hull basket.

The estimated detection capability of the leached-hull monitor is 1 g of U in 1 metric ton of hulls in the presence of 30 Ci of ^{60}Co.

Irradiated Reactor Fuel (Refs. 45 and 46)

The material assayed was irradiated PWR and BWR fuel assemblies with burnups as high as 28,700 MWD/MTU and initial ^{235}U enrichments greater than or equal to 4.0%.

Correlations of ^{134}Cs/^{137}Cs and ^{154}Eu/^{137}Cs ratios, as determined by gamma-ray spectroscopy, with Pu/U ratios, as determined by isotopic dilution techniques or computer calculations, were investigated. A Ge(Li) detector was used to measure segments of whole assemblies in a cooling pond or dissolved fuel solutions. Cesium-137 (662-keV), ^{134}Cs (796- and 802-keV), and ^{154}Eu (1275-keV) peak areas were determined from the multichannel spectra with counting times of 40 to 100 min. Fuel assemblies and solutions were measured over a 4-yr period, and the consistency of certain correlations and gamma-ray ratios was determined.

The reproducibility of the ^{134}Cs/^{137}Cs ratio ranged from 0.5% to 0.8% (RSD) for gamma-ray measurements on dissolver solutions and assemblies for PWR (Trino) and BWR (Garigliano) spent fuel. For the BWR fuel the correlation (^{134}Cs/^{137}Cs)/(Pu/U) varied by 30%. For PWR fuel this ratio was more nearly constant with standard deviations of 1.2%, 1.3%, and 2.0%. The wide range of the BWR values was ascribed to the widely varying power history of the BWR assemblies. Correcting for this factor made the correlation factor much more constant (σ = 3.9%). The ^{154}Eu/^{137}Cs ratio was also measured for PWR fuel with reproducibilities of 1.0%, 5.2%, and 6.8% and (^{154}Eu/^{137}Cs)/(Pu/U) standard deviations of 2.0%, 5.6%, and 8.7%.

The lower values on all triplet values quoted above were obtained from the measurement of solutions with measured Pu/U ratios; the Pu/U ratios for the others were calculated from computer codes.

It was noted that the longer half-life of ^{154}Eu (8.5 yr) versus ^{134}Cs (2.06 yr) makes the ^{154}Eu/^{137}Cs a better correlation to use for safeguards because it is less sensitive to the reactor power history.

5.2.2. Passive Neutron Methods

Passive neutron assay techniques are less sensitive to attenuation in high-Z matrix materials than techniques that use gamma rays. This is of considerable importance for large assay items in which gamma ray self-attenuation can be large. Passive neutron techniques (Sections 5.2.2.2 and 5.2.2.3) are used principally for Pu assay because Pu spontaneous fission neutron emission rates and (α,n) rates are high enough for practical measurements. The (α,n) rates vary with the matrix composition and the degree of mixing of the Pu with the matrix. Coincidence techniques (described in Section 5.2.2.3) that are less affected by the matrix effects have been developed.

5.2.2.1 Slow Neutron Detectors and Instrumentation

Gas proportional counters are used for counting single neutrons and neutrons in slow coincidence. These detectors are gas-filled, cylindrical metal tubes having a center anode wire with a voltage difference applied between the wall and the anode. The fill gas contains ^{10}B or ^{3}He, which have large cross sections for charged-particle-producing reactions with low-energy neutrons. Ions created by the passage of a charged particle or a gamma ray are collected. If the voltage is sufficiently high, ions from the initial ionizing event gain enough energy to further ionize the counter gas, resulting in multiplication of the charge collected. Over a fairly wide range of voltage, called the proportional counter region, the amount of charge collected is proportional to the initial amount of charge. The detectors are surrounded with moderating material, usually polyethylene, to slow neutrons to thermal energies, where ^{10}B and ^{3}He have neutron absorption cross sections of 3840 and 5400 b, respectively. The thermal neutron lifetime in such a moderator may be 20 to 150 μs, the exact time depending on the particular design of the system. Consequently, for coincidence (correlation) counters, the resolving times are of the same magnitude. This is "slow" compared to the "fast" (≈10 ns) timing possible with plastic scintillators (see Section 5.2.3).

The absorption reaction for BF_3 is

$$\begin{aligned} n + {}^{10}\mathrm{B} &\rightarrow {}^{7}\mathrm{Li}^{*} + \alpha + 2.30\,\mathrm{MeV} \quad (94\%) \\ &\rightarrow {}^{7}\mathrm{Li} + \alpha + 2.78\,\mathrm{MeV} \quad (6\%) \end{aligned}$$

The reaction for ^{3}He is

$$n + {}^{3}\mathrm{He} \rightarrow p + t + 765\,\mathrm{keV}$$

where t is a triton. The energies released in these reactions are converted completely into the motion of the charged reaction products. These detectors have low efficiencies for the detection of gamma rays, but they are almost 100% efficient for the detection of the charged particles from the absorption reactions.

For BF_3, the resolution (FWHM divided by the peak value) of the total energy peak of the charged particle can vary from 5% to 40%, depending on the design of the counter. For ^3He, the resolution is 4% to 10%. Typical detector voltages are 1200 to 1800 V for BF_3 and 2000 to 3300 V for ^3He, depending on the gas pressure. Higher voltages are needed for higher pressures.

The BF_3 counter can be filled with gas up to a pressure of 0.10 MPa (1 atm), at which point the gas becomes so dense that some of the initial ions and electrons recombine in the gas before they reach the electrode. Counters with ^3He as the gas can be operated to 0.40 MPa (4 atm) before the gas becomes so absorbing that the thermal neutrons do not penetrate the detector completely. For detection of fast neutrons, higher pressures are useful. The ^3He proportional counters may have Ar added to the gas to increase the stopping power of the detector. Without the added gas, the protons and tritons from the n + ^3He reaction may pass through the gas without losing all their energy. A gas such as CO_2 may also be used to stabilize the counter and to increase the electron drift speed. An activated charcoal coating of the cathode may absorb electronegative gases formed by gamma-ray interactions and improve counter lifetime in a gamma-ray flux (Ref. 51).

Helium-3 counters are more expensive than BF_3 counters but are also more efficient because of the higher cross section. Currently, regulations controlling the shipment of hazardous material cause costs in shipping BF_3 to be higher. Detector diameters of either type range from 1.2 to 5 cm and lengths range from about 25 to 75 cm.

Several detectors may be connected to a common voltage supply and preamplifier when multicounter arrays are used, as is usually the case. The output from the preamplifier is further amplified and then analyzed with an SCA set on the charged particle peak. Banks of detectors may be operated with a coincidence analyzing system, or the output of the single SCA to which the banks are connected may be checked with additional electronics for time-correlated counts. The counters are not damaged by loss of power.

5.2.2.2 Noncoincident Neutron Assay

Description of Method

Neutrons emitted by samples containing SNM originate from two sources: spontaneous fission and (α,n) reactions on low-Z elements (especially O and F but including B, Be, Li, Na, Mg, Al, Si, Cl and C). Both sources can produce additional neutrons by inducing fission in the SNM itself (multiplication). When pure metals are assayed, only neutrons from spontaneous fission (and multiplication) are present. When the SNM is in the form of oxide or fluoride or is mixed with other low-Z matrix materials, both spontaneous fission and (α,n) sources (and multiplication) of neutrons contribute.

A measurement of the total neutron intensity of a sample can be used to assay the amount of SNM present if the neutron detector is calibrated by standards having the same chemical composition, isotopic composition, and matrix material as the assay items. The SNM content of the standards should cover the expected range of SNM content of the unknowns so that multiplication, when present, is automatically included in the calibration. When such standards are not available, the differences between the available standards and the assay items must be determined, and the assay must be corrected for the differences. Because the corrections may be uncertain, coincidence techniques are often used. (See Section 5.2.2.3 and 5.2.3.) The main uncertainty occurs because of the (α,n) dependence on the matrix material, however, coincidence techniques are less sensitive to the (α,n) contribution.

The spontaneous fission neutron yields for U and Pu metals of various isotopic compositions are shown in Figure 5.18. Inspection of this figure shows why pure U is not routinely assayed by this technique: the neutron yield is quite low at all enrichments. For low burnup Pu, the neutron yield from ^{240}Pu predominates, but its relative contribution is reduced by 50% for high burnup material (38,000-40,000 MWD/MTU). The neutron yield increases considerably as ^{238}Pu and ^{242}Pu increase in abundance with burnup.

Because Pu and U often occur as oxides or fluorides or mixed with oxygen-containing materials, (α,n) contributions occur and are significant. For UO_2 the neutron yield is dominated by spontaneous fission of ^{238}U for natural and low-enriched U. (See Fig. 5.18.) For high-enriched U, (α,n) reactions are the dominant source for UO_2, with ^{234}U giving the largest contribution. For UF_6, the (α,n) rates dominate over spontaneous fission rates for all enrichments. The neutron emission rates from UF_6 are dominated by the (α,n) rate from ^{234}U.

The relative amounts of ^{232}U, ^{234}U, and ^{235}U present in recycled U depend on the burnup history and type of reactor and will lead to varying neutron emission rates that will differ from the rates shown in Figure 5.18.

The relative order of total neutron emission rates for Pu, PuO_2, and PuF_4 parallels that for comparable U compounds (fluoride > oxide > metal). The total neutron emission rates of Pu, PuO_2, and PuF_4 are shown for different Pu compositions for increasing burnup (decreasing ^{239}Pu content) in Figure 5.18. For the Pu compounds the (α,n) yield from PuO_2 is comparable to the spontaneous fission contribution, and for PuF_4 the (α,n) contribution is dominant. The presence of PuF_4 as a process impurity in PuO_2 can occur at the 100- to 1000-ppm level and will increase the neutron emission rate by 0.5% to 5%. Ingrowth of ^{241}Am from ^{241}Pu beta decay ($t_{1/2}$ = 14.4 yr) will also increase the neutron emission rate. If ^{241}Pu is initially present at 0.38 weight percent, the ^{241}Am content will grow at about 14 ppm per month. For older PuO_2 or a larger ^{241}Pu content, the ^{241}Am contribution will be correspondingly larger. The Pu neutron emission rates will predominate over U in mixed (Pu,U) oxide samples.

In cases where the total neutron count has been used directly for SNM assay, BF_3 or ^3He proportional counters embedded in moderator material have been used. The total neutron counting rates have also been measured with active and passive neutron coincidence systems to establish corrections to coincidence count rates. (See Sections 5.2.2.3 and 5.2.3.) Holdup assay (described in Section 5.4.2.) is an application of the total neutron counting techniques of this subsection.

Scope of Applications

Passive noncoincident neutron counting (singles) of pure SNM-bearing materials is used for process monitoring or for verification of more accurate measurements. Plutonium metal content can be verified by counting spontaneous fission neutrons. The technique is also used to verify U enrichment of UF_6 in shipping cylinders. (See Section 5.3.2 for more details of enrichment measurement applications.)

This technique has been investigated as an assay method for Pu content of waste and scrap in 55-gal. waste drums and large boxes; however, because of its sensitivity to matrix variations leading to variable (α,n) contributions, passive and active neutron coincidence counting techniques are

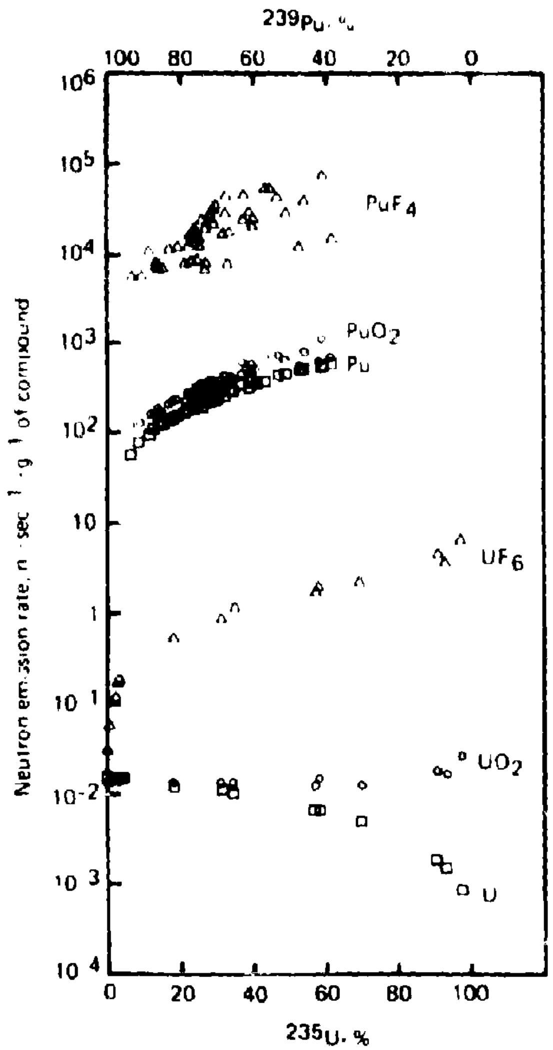

Figure 5.18 Calculated neutron emission rates of U and Pu metals, oxides, and fluorides. Americium ingrowth is not included in data (1-yr ingrowth is expected to increase PuF$_4$ emission rate by up to 10%). Pu isotopics are from a wide variety of reactors (Refs. 52 and 53). Neutron emission rates used in the calculations were obtained from References 53, 54, and 55 and from data supplied by J. Caldwell, Los Alamos National Laboratory.

preferred for assay. Neutron counters are used as monitors for Pu in waste materials to determine whether significant Pu is present to warrant additional recovery procedures.

Holdup measurements of Pu present in process equipment is another possible application of this technique; it is discussed in Section 5.4.2.

Summary of Performance

A summary of the performance of this technique is given in Table 5.16.

Equipment

Several types of detector systems based on proportional counters embedded in moderating material can be used for total neutron counting. One of these types, the neutron well coincidence counter, is discussed in Section 5.2.2.3. The Shielded Neutron Assay Probe (SNAP) and "slab" detectors will be discussed here, and the use of a "cave" detector will be discussed later in this subsection.

The most commonly used detector (Refs. 61 and 62) is the SNAP detector (Fig. 5.19). The detector consists of two ^{3}He proportional counters, 2.5 cm in diameter and 14 to 20 cm long (active region), contained in an inner polyethylene cylinder, 12.7 cm in diameter. This cylinder is surrounded with a 0.8-mm thick Cd sheet as a thermal neutron absorber. A second outer polyethylene shield, about 23 cm in diameter, is used to give the detector modest directional sensitivity. A 120° section of the right circular cylinder is removed from the "front" of the outer polyethylene shield resulting in a front-to-back sensitivity of 4:1 for 650-keV neutrons and 2.25:1 for ^{252}Cf neutrons. The directional sensitivity aids in reducing background from other sources that may be present in the assay area. The SNAP-II detector weighs about 11 kg. The detector with a preamplifier may be connected to a portable electronics unit for signal processing and display. The electronics unit includes a high-voltage supply, an amplifier, two SCAs, two scalers, a timer, and a digital display for the scaler counts. This system detector and electronics are commercially available and cost about $6000.

A slab detector (Refs. 63 through 65) such as is shown in Figure 5.20 consists of one or two rows of BF_3 or ^{3}He proportional counters embedded in a slab-shaped polyethylene moderator. The total detector efficiency is reasonably energy independent when ^{3}He counters were used (as can be seen in Fig. 5.21). The system requires a high voltage supply, a preamplifier, an amplifier, an SCA, and a counter timer.

Table 5.16 Summary of performance: noncoincident neutron assay[a]

				Performance (% RSD)				
Sample Type	Isotopic Composition	SNM Content	Container	Random Error	Systematic Error	Bias	Remarks	Ref.
Pu metal buttons	4.8% to 18.1% ^{240}Pu	1.4 to 2.2 kg	Metal can plus inner bag	2	—	+3 relative to tag values	SNAP detector, multiplication correction	56
	—	1.5 to 2 kg	Metal can plus inner bag	—	—	−10 to −20	SNAP detector, multiplication correction	57
Pu contaminated waste	94% ^{239}Pu, 6% ^{240}Pu	—	8100-L wooden crate	detection limit = 0.7 g for 6-h count			Cave detector	58
MOX waste	91% ^{239}Pu, 8% ^{240}Pu,	0.3 to 200 g	55-gal steel drum	Accuracy = ±25% (2σ) for 1 to 200 g Pu			Slab counter	59
	80% to 90% ^{239}Pu; Pu/(Pu + U) = 3% to 22%	—	55-gal. steel drum	Geometric variations in SNM location could cause 37% error			—	60

SNAP = Shielded Neutron Assay Probe.

[a] All data from literature survey.

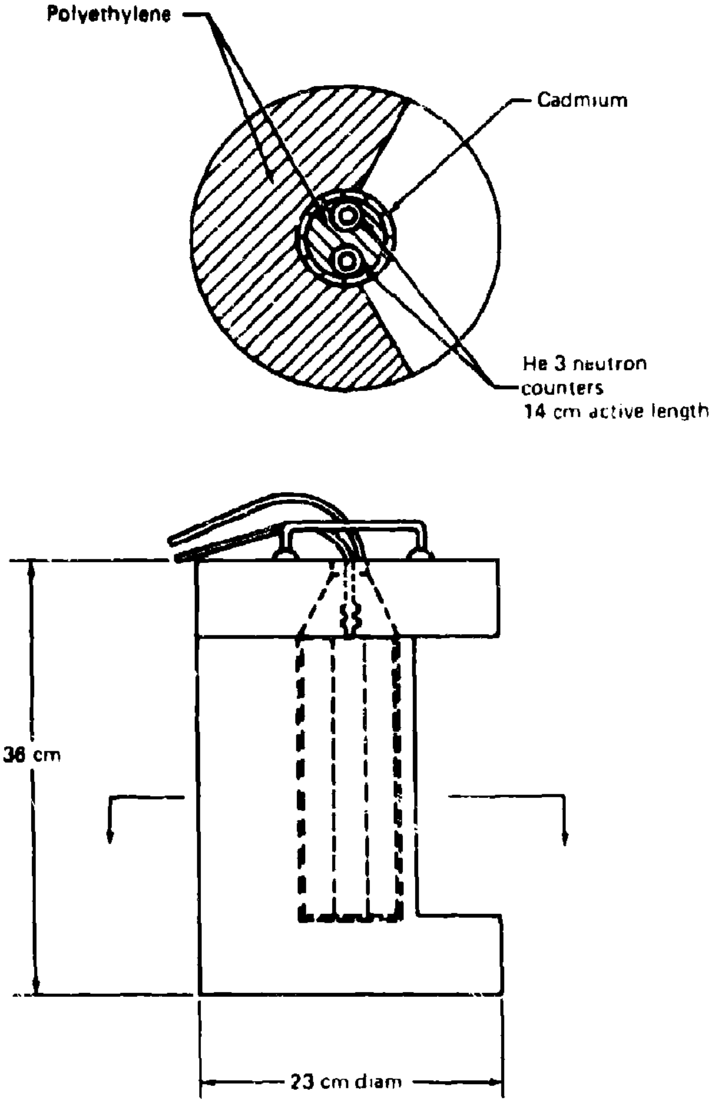

Figure 5.19 Assembly drawing of the portable SNAP detector (Ref. 62).

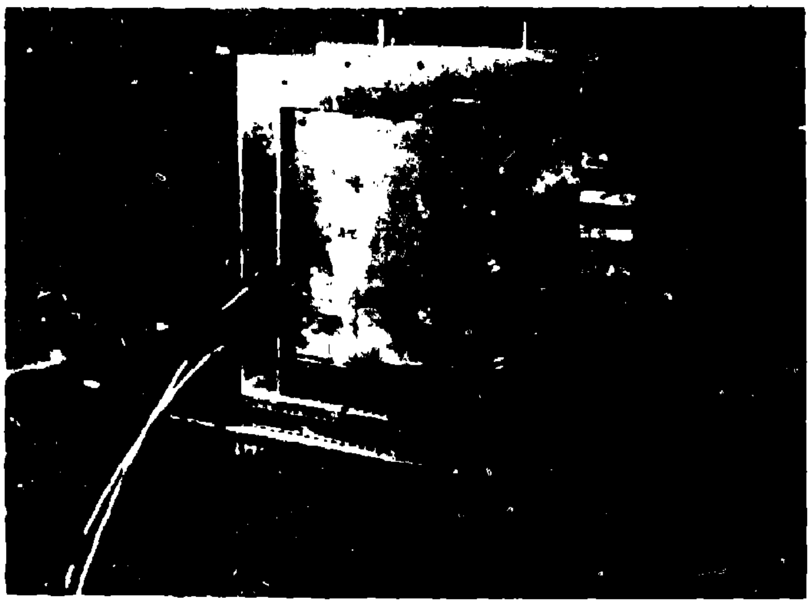

Figure 5.20 Slab detector. (Photograph courtesy of Los Alamos National Laboratory.)

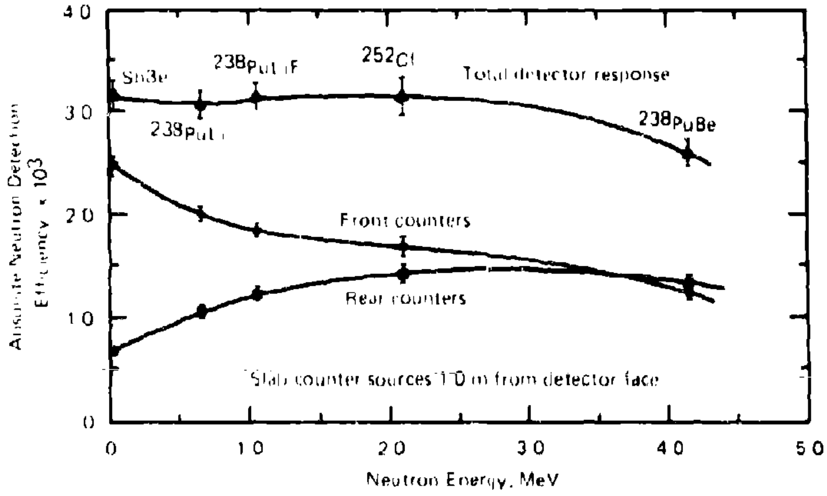

Figure 5.21 Neutron detection efficiency of the detector shown in Figure 5.20

Major Sources of Error

When the assay items are assumed to be Pu metal, the presence of certain low-*Z* matrix material that can produce (α,n) neutrons will cause the assay to be erroneously high. Neutron multiplication in SNM can also have a similar effect for kilogram quantities of Pu. The shape and isotopic composition of the assay item must be known if analytical self-multiplication corrections are to be made. The ratio of total neutrons emitted to spontaneous fission neutrons can be as large as 1.8 for a 6-cm diameter, 2-kg Pu sphere, with 10% ^{240}Pu (Ref. 55). For the same material in the form of a right circular cylinder 1.78 cm high and 8.9 cm in diameter, the multiplication factor is 1.47.

In cases where (α,n) neutrons are known to contribute, nonuniform matrix composition as well as isotopic composition variability can be a source of error. Because the neutron yield depends on the (α,n) reactions in certain low-*Z* matrix materials, the matrix material and SNM must be mixed in the same way throughout the volume (and in the standards). Multiplication caused by (α,n) neutrons can also occur for samples with high SNM content.

Measurement Control Requirements

For pure Pu metal assay, a set of calibration standards, the masses of which span the assay item mass range, should be used. The standards should have the same shape and composition as the samples because multiplication effects can be important. In lieu of standards for the material, the detector efficiency may be measured with in-house neutron sources, and calculations which include multiplication may be done to relate the measured counting rate to the Pu mass.

For assays where (α,n) contributions are present, the calibration standards must closely match the samples in isotopic and matrix material composition. For waste materials this is not always possible, and large uncertainties do occur, but total neutron assay may be the only available technique.

Instruments should be checked at least daily with a normalization source. Background counts should be taken hourly if the apparatus is used in the area where the background can vary because of the movement of source material. For small assay items (less than 100 g of SNM) the calibration curve for SNM (mass as a function of counts/per second) should be linear and can be fit by linear regression. For larger samples, the curve will not be linear, and more sophisticated curve-fitting procedures may be needed.

Data Analysis Requirements

For those analyses for which a calibration curve has been generated with representative standards, the SNM mass of an assay item can be determined by relating the measured count rate (neutrons per second) to SNM mass by the calibration curve. For small quantities of SNM for which a linear response with mass is assumed, the equation relating mass to count rate (CR), assuming a zero intercept, is

$$M = K(\mathrm{CR})(\mathrm{CF}) \tag{5-31}$$

where M is the SNM mass, K is the calibration factor (grams of SNM per neutron per second), and CF is a correction factor for any differences between samples and calibration sources. When possible, chemical analyses of some samples should be performed to determine CF.

Survey of Selected Literature

In this section the first two applications are total neutron assays of Pu metal with no (α,n) neutron contribution. In the rest of the applications, the (α,n) contribution is present.

Pu Metal Buttons (Ref. 56)

A group of 248 Pu metal buttons of known shapes, weighing from 1.45 to 2.20 kg each and having 4.6% to 18.1% ^{240}Pu, was assayed for inventory verification. A second group of 25 buttons, weighing about 2.1 kg each and having 4.8% to 11.9% ^{240}Pu, was also assayed. The buttons were contained in plastic bags inside metal cans.

A SNAP detector was used with sample rotation. Monte Carlo calculations determined multiplication corrections as a function of button height and diameter for cylindrical samples. Empirical expressions based on the calculations were developed. The Pu masses were calculated using the known detector efficiency and isotopic distributions as shown. The detector efficiency was determined with ^{238}Pu-Li, ^{238}Pu-LiF, and ^{252}Cf neutron emission sources. The measurements yielded net counts per second and can be related to Pu mass (M) by the empirically determined equation

$$M = \frac{\Gamma}{2(1-\beta I)}\left[\sqrt{1+\frac{4R(1-\beta I)}{\epsilon\Gamma\nu I'}}-1\right] \tag{5-32}$$

where

$\Gamma = 417.8(d-1.333)^2 + 1757$
d = diameter of button, in.
$\beta = \dfrac{619.5(d-2.673)^2 + 1801}{\Gamma}$
$I = I_0 + I_2$
I_0 = ^{240}Pu isotopic abundance

I_2 = ^{242}Pu isotopic abundance
R = total counts corrected for background
ε = detector efficiency
t = counting time,
y = spontaneous fission neutron yield of ^{240}Pu
I' = $I_0 + 1.71 I_2$

A precision of 2% (1σ) was achieved for 30-s counting periods in a large neutron background (3 mR/h). A bias of 3% from tag values was noted.

Pu Metal Buttons (Ref. 57)

Verification measurements were made on 48 Pu metal buttons weighing 1.5 to 2.0 kg each with known isotopic ratios and each sealed in a metal can. The geometric shapes were initially unknown. The buttons were from two different lots.

A SNAP-II detector was used with a sample rotator. The system was calibrated with one of the buttons taken as a standard. Each button was rotated and counted for 30 s with the detector about 50 cm from the button.

For one lot of 25 buttons, a bias of -20% was found with respect to the tag values. A bias of −10% was found for the other lot. The bias was ascribed to the calibration button whose geometry (spherical) was very different from the rest of the buttons, which were later found to be pancake shaped. The multiplication was higher for the spherical button.

Plutonium Waste (Ref. 58)

The material assayed was Pu (94% ^{239}Pu, 6% ^{240}Pu) calibration standards in 1.3- by 1.3- by 2.1-m wooden crates. The system is designed to assay Pu-contaminated combustibles, contaminated machine tools, gloveboxes, and other crated material weighing from 400 to 2000 kg.

A "cave" detector (Fig. 5.22) was designed to assay very large pieces of equipment (such as gloveboxes) to be sent to waste disposal. Ten detectors, 30.5 cm in diameter, made of Li-loaded ZnS scintillators were mounted on the walls, ends, bottom, and top of a polyethylene cave large enough to accommodate boxes 1.5 by 1.8 by 3.0 m. Large pieces of equipment could be loaded into the cave and assayed for Pu by detecting the scintillations caused by neutrons interacting with the Li. One additional detector shielded from the cave interior was used to monitor background. The signals from the 10 scintillators (each coupled to a 12.7-cm diameter PM) are combined into three groups for counting. The detector response as a function of position was plotted by moving four 25-g Pu samples to different locations in the cave.

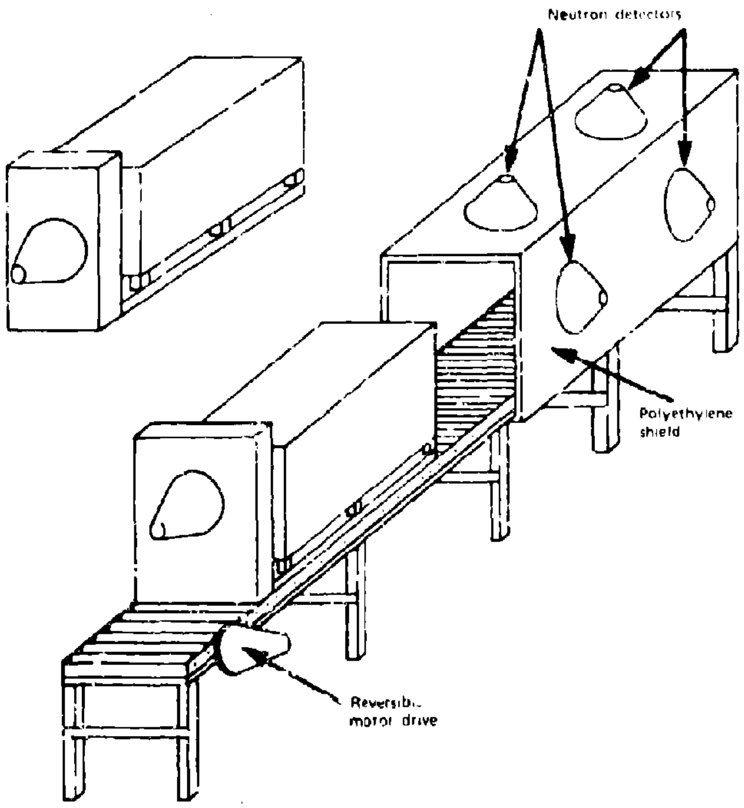

Figure 5.22 Cave detector. (Figure courtesy of Rockwell International, Rocky Flats Plant.)

The system could detect 4 g of Pu concentrated in the center of a crate with a 6-h counting time. It could detect 0.7 g at the 95% confidence level for 6-h counting periods or 10 g counted for 20 min for Pu uniformly distributed throughout the volume.

MOX Waste (Ref. 59)

The material assayed was MOX in waste drums. The Pu isotopic distribution was 90.97% ^{239}Pu, 8.16% ^{240}Pu, with a Pu/(PuO_2 + UO_2) ratio of 0.24. The masses of Pu per container ranged from 0.3 to about 200 g.

A slab counter was used with one set of five BF_3 detectors mounted on top of an identical set of detectors. They were embedded in paraffin and used to assay 55-gal. waste drums, which were rotated. Each set of detectors had its own power supply, preamplifier, amplifier, SCA, and scaler. The sum of the scalers was taken to be proportional to the amount of Pu present. A calibration standard of 13 g of PuO_2 of known isotopic distribution in a 0.5-L container of "typical" organic matrix material (sugar) was placed in an empty 55-gal. drum. A calibration equation of the form of Eq. 5–31 was used.

The estimates of the solid waste assay accuracies (2σ) were given as 25% for 1 to 200 g of Pu.

MOX Waste Standards (Ref. 60)

The MOX waste standards in 55-gal. drums were assayed. The standards were sealed in plastic bags packed with shredded cloth that were placed in 4-L metal cans. The cans were then placed in three vertical cylinders within a 55-gal. drum, four cans to a cylinder, and shredded cloth was placed around the cylinders. The SNM loading of a cylinder could then be changed conveniently by exchanging the metal cans with one containing different amounts of MOX. Waste standards (25 cans) were loaded with MOX containing 0.55 to 6.2 g Pu with an isotopic composition of 80% to 90% ^{239}Pu, the rest being mainly ^{240}Pu. The Pu/(Pu + U) ratios used were 21.6%, 3.9%, and 2.9%.

A slab detector that had two rows of ^{3}He detectors embedded in polyethylene was used. The system had 13 detectors and an efficiency of 10% to 15%. The ^{3}He detectors were 2.5 cm in diameter and 61 cm long and were filled to a pressure of 0.5 MPa (6 atm). The drum being assayed was placed close to the detector but was not rotated. Geometrical variations could cause as much as a 37% error for nonuniform Pu loadings.

5.2.2.3 Thermal Neutron Slow Coincidence Techniques

Description of Method

A thermal neutron slow coincidence system is used for nondestructive assay of Pu-bearing material by measuring the coincidence rate of thermalized fission neutrons from Pu. The coincidence requirement frees the assay from the interference caused by (α,n) reactions on low-Z elements in the matrix. The (α,n) neutrons appear randomly, and accidental coincidences from these neutrons constitute a background to the fission neutron coincidence rate. For small masses of Pu (less than 200 g), the coincidence rate is proportional to the amount of Pu present. For larger masses either a number of calibration standards or another means for correcting neutron multiplication is required. For example, the article by N. Baron (Ref. 66) provides a multiplication correction for a dual-ring coincidence counter.

The neutron coincidence system is "slow" because the coincidence interval is ten's of microseconds, rather than nanoseconds, as is the case for "fast" coincidence systems. The slow systems operate by moderating high energy neutrons from spontaneous fission to thermal energies where they can be detected with high efficiency. Neutrons emitted upon spontaneous fission of SNM escape from the sample and are thermalized in the moderating material of the detector. The thermal neutron flux in the detector decays at a rate dependent on leakage and absorption. The average lifetime of a neutron in the detector (die-away time) is characteristic of a particular detector system and ranges from about 50 to 200 μs. Neutron detectors, BF_3 or ^3He proportional counters, embedded in the moderating medium are used to count the thermal neutrons.

Coincidence methods used by these detector systems are based on the facts that real neutron coincidences occur during the thermal neutron die-away time following the fission event and accidental coincidences occur constantly at a uniform rate. After a neutron is detected, the system counts the number of subsequent neutrons F_i, for a specified time W, normally a die-away time. The system then waits several die-away times after each detected neutron and counts the number of neutrons B_i in an interval of width W. F_i and B_i are accumulated in scalers over the time of measurement, with results F and B, respectively. The net number of coincident counts N can be written:

$$N = F - B \tag{5-33}$$

For a given measurement time, N is proportional to the amount of spontaneously fissioning material present. This method is called the coincidence gate method. Through calibration with known standards, the amount of SNM can be determined. This coincidence technique may also be called a correlation technique because the time correlation between neutrons is measured. This can be emphasized by noting that a single proportional counter with moderator can be used as the detector for this technique.

There are several variations of the coincidence gate method. The total number of neutrons counted per second G may be used to correct the coincidence rate for accidental coincidences, assuming the background to be constant. In this case, instead of adding the number of neutrons detected in gates of width W following each neutron detected, the rate of gates N' is the number of real plus accidental coincidence gates per unit of time. The rate of accidental coincidence gates that would occur if there were no correlated neutrons may be calculated from G using statistical methods. The result of subtracting this accidental rate from N' is

$$N = N' - \frac{G^2We^{-GW}}{2} \cong N' - \frac{G^2W}{2} \tag{5-34}$$

where N is approximately proportional to the amount of fissionable material. This calculated accidental coincidence correction is not accurate at count rates for which $GW > 0.1$.

A second method for establishing the fission rate uses a shift register as a solid-state delay line to determine for each neutron the number of neutrons that have preceded it in the prior time interval of width W; this is the number of real plus accidental coincidences F_i. The same correlation is also established with those neutrons that have occurred in the time interval W that occurred in the preceding 1000 μs or so; this is the number of accidental concidences B_i. The difference between the shift register method and the coincidence gate method is that the gate method fails when there is a significant probability of overlapping gates, whereas the shift register method can accommodate overlapping correlation intervals. This shift register method can accommodate much higher count rates, up to 100,000 counts/s. The use of this technique is discussed by Zucker (Ref. 67). Electronic techniques for determining the net coincidence rate are reviewed by Ensslin, Evans, Menlove, and Swansen (Ref. 68).

All these systems are used for Pu assay, and the assay result is commonly quoted in terms of the mass of "effective ^{240}Pu." Equation 5–35 (Ref. 69) gives the effective mass:

$$^{240}M_{\text{eff}} = {}^{240}M\left[1 + 2.82\ \frac{^{238}M}{^{240}M} + 2 \times 10^{-5}\ \frac{^{239}M}{^{240}M} + 2.4 \times 10^{-5}\ \frac{^{241}M}{^{240}M} + 1.91\ \frac{^{242}M}{^{240}M}\right] \tag{5–35}$$

where ^{i}M is the mass of the ith isotope, and the numerical coefficients are the ratios of the spontaneous fission neutrons emitted per second per gram for the isotopes divided by that for ^{240}Pu. The values for ^{238}Pu and ^{242}Pu have been adjusted to conform with preliminary values recommended for spontaneous fission data by IAEA (Ref. 70). This definition of effective ^{240}Pu mass does not account for the different average multiplicities ($\bar{\nu}$) of neutrons emitted in spontaneous fission by different isotopes. The values of $\bar{\nu}$ for ^{242}Pu and ^{240}Pu (2.14 ± 0.009 and 2.151 ± 0.006, respectively) are indistinguishable; and this effect is small unless the ^{238}Pu ($\bar{\nu} = 2.21 \pm 0.07$) content is greater than 3% of the ^{240}Pu content.

Scope of Applications

Plutonium or MOX in fuel plates, fuel pins, powder, pellets, scrap, and waste can be assayed by this method. Samples containing from 0.5 g to 200 g of effective ^{240}Pu (5 g to 2000 g of Pu with 10% ^{240}Pu) can be measured. Slow coincidence counting systems have been designed to measure objects ranging in size from small fuel pins to 55-gal. drums. The detector systems are available in several sizes to accommodate this range of container sizes. One type of coincidence counter, the High-Level Neutron Coincidence Counter (HLNCC), is adjustable to accommodate containers larger than 18 cm in diameter and is capable of assaying samples containing several kilograms of Pu. Kilogram quantities of LEU can be measured using ^{238}U spontaneous fission neutrons.

Summary of Performance

A performance summary is given in Table 5.17.

Equipment

Slow coincidence counting systems have been made with two types of detector arrangements, single ring or double ring, depending on the arrangement of the proportional counters. Single-ring counters may be portable, such as the HLNCC, or stationary, such as a larger, efficient Neutron Well Coincidence Counter (NWCC) (Refs. 69 and 76). An example of a NWCC is shown in Figure 5.23; an HLNCC is shown in Figure 5.24. A double-ring counter has two rings of counters that can be used as two separate banks of detectors or used together (Ref. 66). There is a difference in the moderation of the neutron flux that reaches each of the two detector banks that can be exploited to make corrections for moderation and multiplication in the assay item.

For the single-ring NWCC's the proportional counters are typically connected in parallel to the high-voltage supply and to a preamplifier. The preamplifier output is amplified and routed to the correlation unit. To reduce pulse pileup caused by high count rates, the 18 proportional counters of the HLNCC are divided into six groups of three, each having its own preamplifier, amplifier, and discriminator. The amplifier outputs are then summed and sent to a single correlation counting unit operating on the shift register concept. Dual-ring counters have separate electronics for each ring of detectors.

The characteristic die-away times of all these detector systems can be reduced by the insertion of neutron-absorbing Cd in the moderator, which also reduces the detection efficiency. In one case the die-away time changed from 84 to 42 μs with the partial covering of the detectors, and to 4 μs with complete covering, while the efficiencies decreased from 18.5% to 8.2% and to ≈0.8% respectively (Ref. 69). Reduction of the die-away time allows the counting of items with larger effective ^{240}Pu mass. A dual-range detector (see Fig. 5.25) is one that allows the addition of Cd sleeves in the moderator to increase the range of Pu masses that can be measured. Another method of reducing the sensitivity to accommodate larger masses is to disconnect some of the proportional counters.

Table 5.17 Summary of performance: thermal neutron slow coincidence techniques

Sample Type	Isotopic Composition	SNM Content	Container	Volume	Counting Time	Random Error	Systematic Error	Source[a]	Ref.
PuO_2 waste	94% ^{239}Pu, 6% ^{240}Pu	—	Steel drum	55 gal.	—	"Background ≤10 mg ^{240}Pu"		L	71, 72
MOX fuel rods 13% and 26% Pu	87% ^{239}Pu, 11.5% ^{240}Pu	11.8 or 23.4 g	Fuel rod	0.95 by 15.2 cm	60 min	1.4	—	L	73
PuO_2	11.9% ^{240}Pu	900 g	Metal can	—	100 s	4.5	—	L	74
Pu in residues	11% to 12% ^{240}Pu	8 to 10 g	Metal can	—	—	9	—	L	74
PuO_2	9% ^{240}Pu	30 to 150 g	Metal can	1 qt	500 s	4.4 at 96 g	3.0 at 111 g	U	
PuO_2 in compacted waste	8% ^{240}Pu	0 to 40 g	Plastic bag	29 L	500 s	7.6 at 12 g	5.6 at 28 g	U	
PuO_2 in plastic waste	8% ^{240}Pu	0 to 20 g	Cardboard carton	2 L	10 min	11 at 2 g	13 at 2.6 g	U	
Uranium residues	<5% ^{235}U	0.14 to 31 kg	Metal can	7.6 L	200 to	≈5 at ≈11 kg	—	L	75
					1000 s	≈10 to ≈15 at ≈1 kg	—	L	75

NWCC = neutron well coincidence counter.

[a] L = literature survey; U = users' survey of production facilities.

Figure 5.23 Neutron Well Coincidence Counter (NWCC). (Photograph courtesy of National Nuclear Corp.)

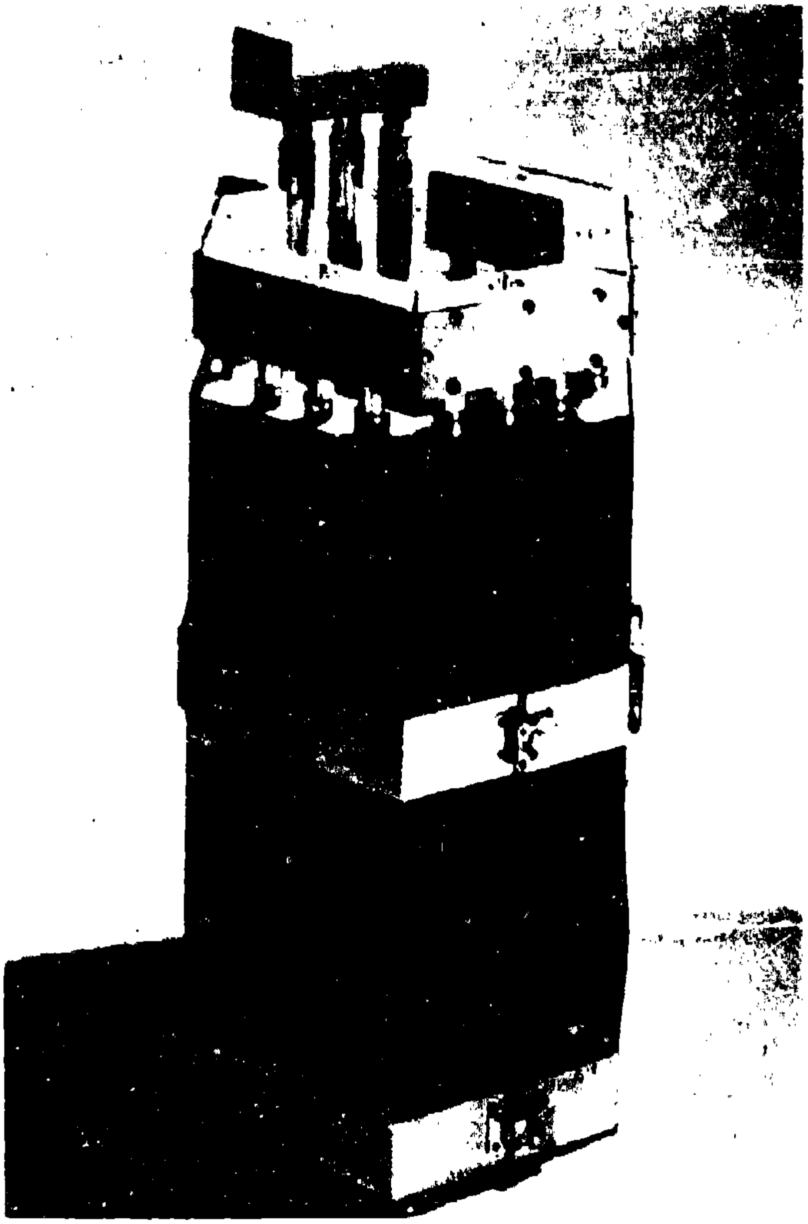

Figure 5.24 High Level Neutron Coincidence Counter (HLNCC) (Photograph courtesy of IRT Corp.)

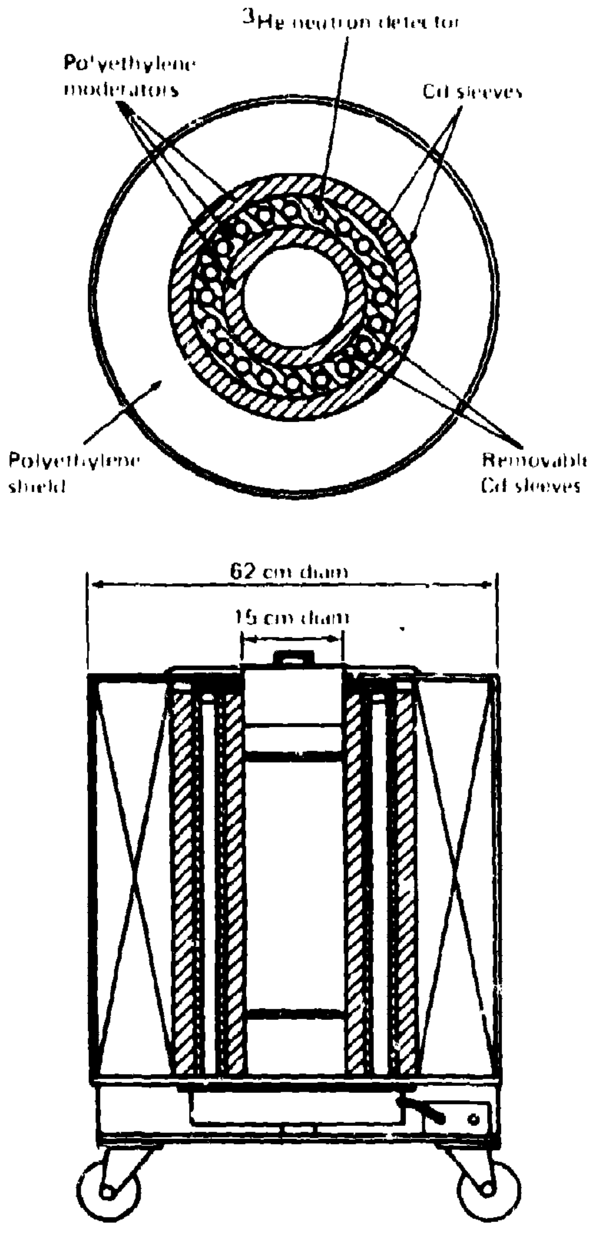

Figure 5.25 Dual range neutron coincidence counter for the assay of plutonium samples in the mass range from 1 to 2000 g (from Ref. 77).

Cadmium may also be used to line the inside and outside of the well. The inside lining reduces multiplication because thermal neutrons from the moderator cannot return to cause further fissions in the sample. The outside liner reduces room background by absorbing the external thermal neutron flux.

The cost of an NWCC system ranges from $40,000 to $80,000, depending on the size of the counter. This cost includes the counters and electronics. Some systems use an additional small programmable calculator for some of the calculations.

Major Sources of Error

As with other NDA methods, systematic errors can result if material characteristics of the physical standards used for calibration differ significantly from those of the samples measured.

Because neutrons from the spontaneous fission of ^{240}Pu are the major source of coincidences, variations in its isotopic content from the physical standard values cause a nearly proportional error in the assay. For example, a 10% variation in ^{240}Pu isotopic content will cause a 10% variation in the ^{240}Pu effective mass for low burnup Pu (93.6% ^{239}Pu, 5.9% ^{240}Pu).

Variations of Pu location in the sample may cause shifts in the response of the instrument. A systematic shift of 10% was noted when a ^{252}Cf neutron source was moved 3.5 in. along the radial direction, or 4 to 5 in. up from the bottom of the container for an 8-in. diameter well counter (Ref. 69). Such changes in sensitivity may cause the instrument response to be significantly dependent on fill height in a container.

The neutron multiplication factor of the sample depends on the amount of fissile Pu, the Pu geometrical configuration, the amount of moderator present, and the particular configuration of the detector system. The multiplication factor increases with the amount of Pu in the sample. This effect is indicated by a positive curvature in the calibration curve (coincidence counts as a function of mass). The geometric configuration of the Pu in the sample can also affect the multiplication factor. For example, an increase of 23% in the coincidence count rate for the HLNCC was measured for pairs of ZPPR fuel plates as they were moved from 12 cm apart to contact (Ref. 76). Neutron moderation by hydrogenous matrix material can also increase the induced fission rate. An increase of 1% to 6% for coincidence counts from a ^{252}Cf source occurred with the addition of polyethylene chips to various matrices containing sand, ash, and MgO. Matrix-generated (α,n) neutrons can also induce fissions, increasing the neutron coincidence rate. If the sample is not surrounded by Cd shielding, moderated thermal neutrons may cause increased multiplication by being scattered back into the sample and inducing more fissions. Calculational methods for correcting for moderation and multiplication will be discussed.

The presence of matrix materials with high neutron cross sections may also cause excessive self-absorption of the neutron flux and a biased result.

Measurement Control Requirements

Physical standards traceable to primary reference materials have not been used for the calibration of these systems because the matrix sensitivity of the assay requires the in-house standards to be as close in isotopic and matrix composition to the samples as possible, and appropriate reference materials generally do not yet exist. Standards should be measured at least weekly, and a ^{252}Cf source should be used for daily normalization.

A range of standards (at least four) is required to describe adequately the calibration curve. If the samples and standards have identical isotopic compositions, then the calibration can be made in terms of total Pu. In general, the calibration curve will not be linear, especially if multiplication and self-absorption occur. If the standards do not match the samples closely, the effect of the differences must be determined. This may be done through calculations or may require destructive analysis of a typical sample. In the case of the double-ring counter, the correction may be determined by analysis of the differences in the inner and outer ring count rates.

Data Analysis Requirements

The data analysis depends on the type of electronic circuitry used for the determination of the net neutron coincidence rate N. Two approaches were exemplified in Eq. 5–33 and 5–34. These systems have a dead-time error for the length of time that the amplifier is busy shaping a pulse. The correction for dead-time is complex.

For other systems, additional data for the particular sample type are needed to relate net counts to mass of ^{240}Pu. The corrected coincidence rate N_{corr} for Pu metal and PuO_2 powder for the HLNCC (Ref. 76) is given as

$$N_{corr} = \frac{N\varrho}{M\varrho_m} \qquad (5\text{–}36)$$

where ϱ is the ratio of net to total counts N/G for a small nonmultiplying sample, ϱ_m is the ratio N/G for a small multiplying sample, and M is the multiplication correction factor that is a function of the average neutron multiplicity, the ratio of (α,n) neutrons to spontaneous fission neutrons and multiplication.

The magnitude of the multiplication correction can be significant. In one application for a series of PuO_2 samples, the magnitude of the multiplication correction steadily increased with increasing PuO_2 sample mass, growing to a factor of 1.8 for a 500-g mass of PuO_2. With the correction, the response curve (relative coincidence counts per gram of effective ^{240}Pu as a function of PuO_2 mass) is flat to within ±3% for 20 to 500 g of PuO_2 (Ref. 76).

For the double-ring counter, the effective ^{240}Pu mass ^{240}M is given by

$$^{240}M = \left[\frac{N_I + N_O + 2\sqrt{N_I N_O}}{(G_O/G_I)^{3.295}(N_I/N_O)^{2.255}(31.45)}\right]^{1/1.065} \tag{5-37}$$

where I and O stand for the inner and outer rings and G and N for total and net counts. This empirical equation holds for PuO_2 powder mixed with MgO, SiO_2, and a moderating (hydrogenous) material (Ref. 66).

Several formulas for the one-shot circuit are given by Sher (Ref. 69) for correcting for amplifier dead-time, moderation, and geometry effects. When the system is operated in the live-time mode (where time is counted only when the coincidence gate is closed), the corrected total count G_{corr} is

$$G_{corr} = \frac{G_O t_c / t_\ell}{1 - DG_O/t_\ell} \tag{5-38}$$

where G_O is the measured total count, t_ℓ is the live time, t_c is the clock time, and D is the amplifier dead time. The corrected value of the net coincidence counts N_{corr} is

$$N_{corr} = \frac{N_O}{\left(1 - DG_O/t_\ell\right)^3} \tag{5-39}$$

where N_O is the value of the observed coincidence counts for live time t_ℓ. The ratio G^2_{corr}/N_{corr} can be shown to be insensitive to moderation and geometry effects and proportional to the fission rate. Thus, this quantity can also be used for assays by calibrating with standards that have the same relative (α,n) contribution as the sample but do not necessarily have the same geometry or moderator composition. In one experiment where almost 6 kg of polyvinylchloride (PVC) was added to a sample, G^2_{corr}/N_{corr} was insensitive (±3%) to the amount of PVC added, while N_{corr} varied by 15% with changing amounts of PVC (Ref. 67).

Survey of Selected Literature

Plutonium Scrap and Waste (Refs. 71 and 72)

Plutonium (94% ^{239}Pu, 6% ^{240}Pu) scrap and waste in 55-gal. drums and smaller containers was assayed.

A large, 15% efficient (for total neutrons) NWCC consisting of seventy-eight 5.0 cm in diameter BF_3 proportional counters embedded in slabs of polyethylene was used. The NWCC was located in a 60-cm thick water shield. The counters were all connected in parallel to a preamplifier and an amplifier. A shift register coincidence circuit was used, and the counting times were 180 s per sample. In-house calibration standards were used.

The total and coincidence counting rates were 15.2 and 0.6 counts/s per gram Pu (5.8% ^{240}Pu), respectively. The corresponding background counting rates were 3.9 and 0.16 counts/s, respectively, at sea level and about 4 to 6 times higher at an altitude of 2.2 km because of cosmic-ray interactions. The coincidence background at sea level is less than or equal to 10 mg of ^{240}Pu. The point-to-point spatial response varied within ±10% of the volume-averaged response. Addition of polyethylene as matrix material at a density of 0.2 g/cm^3 reduced the volume-average response by 42% and caused large response variations (up to ±30%).

MOX Fuel Rods (Ref. 73)

Zero power reactor (ZPR) fuel rods loaded with MOX pellets were assayed. There were two different loadings: Type F—$(U_{0.85}, Pu_{0.15})O_2$ and Type G—$(U_{0.70}, Pu_{0.30})O_2$. The Pu isotopic composition was ^{238}Pu (0.05%), ^{239}Pu (86.55%), ^{240}Pu (11.5%), ^{241}Pu (1.70%), and ^{242}Pu (0.2%). The rods were 0.95 cm in diameter and 15.2 cm long and contained 11.8 and 23.4 g of Pu for the F and G types, respectively.

The configuration used for this NWCC was six BF_3 proportional counters surrounded by polyethylene with a small well for a fuel rod. For each type of loading, several rods were counted then destructively assayed to establish the calibration relationship of count rate to mass of plutonium. In all, 237 rods were assayed, each for 60-min count times. The rods were randomly selected from a total of 19,065.

Because the isotopic composition of the 237 rods was known, the results of the assays could be compared with the known contents of the 120 rods that were assayed chemically. The coefficient of variation for a single NDA measurement of a rod was 1.4%. The average Pu contents of the Type F rods were 13.35 ± 0.06 and 13.19 ± 0.02 weight percent Pu for NWCC and chemical assay methods, respectively, and of the Type G rods were 26.26 ± 0.07 and 26.48 ± 0.04 weight percent Pu. These averages indicate that the NWCC had a bias of +1.2% for the F-type rods and −0.8% for the G-type.

In-Line Measurement of PuO_2 Powder and Scrap (Ref. 74)

Plutonium (11 to 12% [illegible]) in process residues (9 g Pu per can) and PuO_2 powder (1 kg PuO_2 per [illegible] [illegible]ssayed.

The detection system con[illegible] a ring of fifteen ^{3}He proportional counters, surrounded by a polyethylene moderator with a 16-cm well diameter and located in a process line. Cans located in a glovebox were raised into the counter. An external Cd liner and additional polyethylene were used to shield the NWCC from external background, while an internal Cd liner was used to reduce induced fission. This detector was designed for high sensitivity (a few tenths of a gram) measurements of scrap material. Cans containing 1 kg of PuO_2 were assayed by counting with only five of the proportional counters.

Chemical assays were available for total Pu comparisons with the NDA technique. The total mass of 10 of the 9-g assay items was 87.29 g of Pu by the chemical analysis and 86.86 g of Pu by the NWCC method. The scatter of the NDA values about the analytical values indicates a relative standard deviation of 9% with no detectable bias. Nine cans, each containing about 900 g, were each counted for 100 s, with a counting statistics uncertainty of 4.5% for each measurement. The relative standard deviation based on nine items was 4.6%, indicating that counting statistics was the major source of random error. The average mass of Pu was 888 ± 40 g compared with the analytical value of 874 g.

Uranium Residues (Ref. 75)

LEU ($\leq$5% ^{235}U) residues in 16-cm diameter and 47-cm long cans were measured. Container contents ranged from 0.16 to 31 kg U.

'Heavy' cans (typical weight $\cong$ 11 kg) were placed in a thermal neutron coincidence counter and counted for 200 s; light-weight cans (typical weight $\cong$ 1 kg) for 1000 s. The counter consisted of eighteen ^{3}He detectors with a variable gate coincidence circuit. Results were compared with stated values.

Seventy-two cans were measured, indicating a total of 508 kg of ^{238}U compared with an assigned value of 490 kg, a difference of 3.5%. For the heavy cans, a random error of $\approx$5% RSD was observed, and for the light-weight cans, the relative standard deviations ranged from 10% to 15%.

Survey of Production Facilities

Neutron well coincidence counters (built by National Nuclear Corp.) were used to measure the Pu content in MOX powder present in waste and scrap materials through the spontaneous fission of the even-numbered isotopes of Pu. The ^{240}Pu weight fraction was 8% Two separate systems were used, one designed to measure packages up to 2 by 2 by 1 ft and the other to measure smaller containers. Table 5.18 lists the random error performance of these systems. The last column gives the number of 2-month periods during which the data were collected. The random errors were calculated from duplicate runs on process materials, typically 15 duplicates per 2-month period.

The systematic errors for these materials are shown in Table 5.19 for the same counting times. The systematic errors quoted are calculated from multiple measurements of calibration standards taken over a 6- to 8-month period. The calibration curve used is of the form $y = bx$, where y is the instrument response and x the known Pu content. The instrument response is the corrected net counts (CN) calculated from CN = $R - G^2T_1/T$, where R = register counts, G = gross counts, T_1 = 64 μs (gate), and T = count time.

Four to six standards were used to define the calibration curve. The MOX powder standards consist of powder that was analyzed chemically; standards for contaminated plastics and compacted waste were produced by dispersion of MOX through a representative matrix. SNM loadings spanned the values observed in unknowns. One standard was counted for every assay. The well counters were in use for 4 yr.

5.2.3 Fast Coincidence Methods: Fast Neutron and Gamma-Ray Coincidence Assay

Active systems using fast coincidence techniques (see Chap. 6) have been developed that can also be used for the passive assay of Pu. This section is a discussion of these systems used in the passive mode.

Description of Method

Nondestructive assay of SNM that undergoes spontaneous fission can be accomplished by fast coincident detection of neutrons and/or gamma rays. When fission of a nucleus occurs, approximately two to three neutrons and five to seven gamma rays are emitted simultaneously. Radiation escaping from the sample interacts with one or several large organic scintillators that are sensitive to both neutrons and gamma rays. Light is generated in the plastic scintillators by fast neutrons, mainly through elastic collisions with hydrogen nuclei, and by gamma rays, mainly through interactions with the atomic electrons. Photomultipliers are coupled to the scintillators to transform the light into an electronic signal.

If two detectors view the fissioning material, the detector signals can be checked to see if neutrons and gamma rays arrived at the detectors at essentially the same time. In a common electronic configuration the signal from the detector is sent to an SCA where the signal height is required to be within lower and upper discriminator levels. The lower level is used to eliminate small pulses resulting from background and noise, and the upper

Table 5.18 Plutonium scrap materials, random error

Material	Pu content (g)	Counting Time (s)	Weight at Evaluation (g Pu)	No. of 2 Month Collection Periods	Random Error (% RSD)
MOX powder in 1-qt can	30 to 150	500	96.2	5	4.4
MOX in bagged plastic waste in 4 ¾-in. outer-diameter by 8-in. cardboard container	0 to 20	600	1.9	5	10.9
MOX in compacted combustible waste (40 to 50 lb) in 10-by 10-by 18-in. paper bag in plastic bag; counted in larger well counter.	0 to 40	500	12.5	4	7.6

Table 5.19 Plutonium scrap materials, systematic error

Material	Weight at Evaluation (g Pu)	No. of 2-Month Collection Periods	Systematic Error (% RSD)
MOX powder	111	3	3.0
MOX in plastic waste	2.6	3	12.6
MOX in compacted waste	28.5	4	5.6

level is used to eliminate higher energy background. If the signal falls within the discriminator window, the discriminator generates an output pulse of constant height and width τ.

Pulses from two discriminators that overlap in time are said to be in coincidence; this coincidence network has a resolving time of 2τ. In common applications of coincidence systems, there are many more pulses that are noncoincident. If C_1 and C_2 are the total count rates for detectors 1 and 2, the accidental coincidence rate is $2C_1C_2\tau$. To reduce the accidental coincidence rate, the resolving time should be as small as possible. For organic scintillators used to detect gamma rays and neutrons, resolving times may be "fast" (5 to 100 ns) depending on the application.

Usually double or triple coincidence requirements are used for assay with two or more detectors. A quadruple coincidence requirement is possible, but the resulting counting rates are small, and long counting times are required for 1% statistics. Use of a multiple coincidence system considerably reduces the background resulting from other types of radioactive decay and (α,n) reactions on matrix material.

Several systems have been developed to use fast coincidence assay, but these differ in their emphasis on neutron-neutron, neutron-gamma, or gamma-gamma coincidence. If any of these systems is made less sensitive to low-energy neutrons or low-energy gamma rays (or both) by use of absorbers, then it will be less sensitive to uncertainties resulting from matrix attenuation effects; however, the counting rates will be lower.

Scope of Applications

This technique can be used to assay Pu containing 0.05 to 50 g of ^{240}Pu in a wide variety of forms including oxide, MOX, scrap, and waste. Assay of ^{238}Pu is another possible application. The spontaneous fission rates of ^{235}U, ^{238}U, and the odd isotopes of Pu are too low for most practical measurements.

The instruments are available in a range of sizes that can accommodate cans with diameters up to 30 cm and heights up to 130 cm. Several models are designed for 55-gal. waste drums.

Summary of Performance

A performance summary is given in Table 5.20.

Equipment

Several fast plastic scintillators form a well into which the sample is placed. (See Fig. 5.26 for a line drawing of a Random Driver, a typical fast coincidence system.) A photomultiplier, power supply, and preamplifier are needed for each scintillator. Fast-timing coincidence electronics and scalers are also required. A programmable calculator has been interfaced to most systems for calibration and assay calculations. The sample may be rotated and translated.

A fast coincidence requirement of 50 to 100 ns is used for multiple coincidences: twofold, threefold, fourfold, or higher coincidences can be used, as well as singles, depending on the application. The counting rates decrease for the higher multiplicities; twofold and threefold coincidences are commonly used. The threefold coincidence has a lower count rate than does a double coincidence system but is less sensitive to background. The multiplicity ratios can be used for an attenuation correction.

Different sample sizes can be accommodated either by using the appropriately sized detector system, by moving the detectors to adjust for larger or smaller diameters, or by translating the sample. The Isotopic Source Assay System (ISAS) shown in Figure 5.27, Isotopic Source Adjustable Fissometer (ISAF), and Random Driver (RD) are commercially available systems that can be used for these measurements. The cost of this type of system is from $100,000 to $140,000. See Chapter 6 for a discussion of these instruments used in the active mode.

Major Sources of Error

Matrix effects, self-absorption, and multiplication all can cause errors in the assay determinations. All these effects can lead to large systematic errors when the calibration standards are different in composition and in matrix material from the samples measured.

Hydrogen-containing matrix material can cause an incorrect assay by degrading spontaneous fission neutrons to energies below the detector threshholds. Neutron-absorbing or neutron-moderating material can also change the amount of neutron multiplication. High-*Z* matrix material or a large amount of SNM can reduce the spontaneous fission gamma-ray intensity by attenuation.

Table 5.20 Summary of performance: fast neutron and gamma-ray coincidence assay[a]

Sample Type	SNM Content	Container	Counting Time (min)	Performance (% RSD) Random Error	Performance (% RSD) Systematic Error	Remarks	Ref.
Metal plates 0.025 cm thick, 93.4% ^{239}Pu, 6% ^{240}Pu	0.5 to 5.0 g ^{240}Pu	—	—	—	—	Isotopic Source Adjustable Fissometer system (ISAF)	78
PuO$_2$	0.1 to 0.3g ^{240}Pu	0.5-L metal can	10	System detection limit = 10 mg ^{240}Pu		Random Driver designed for small samples	79
Pu in combustible scrap	0 to 60 g Pu	208-L metal drum	5	16 (for 0.16 g of ^{240}Pu)		Fission multiplicity detector	80

[a] All data from literature survey.

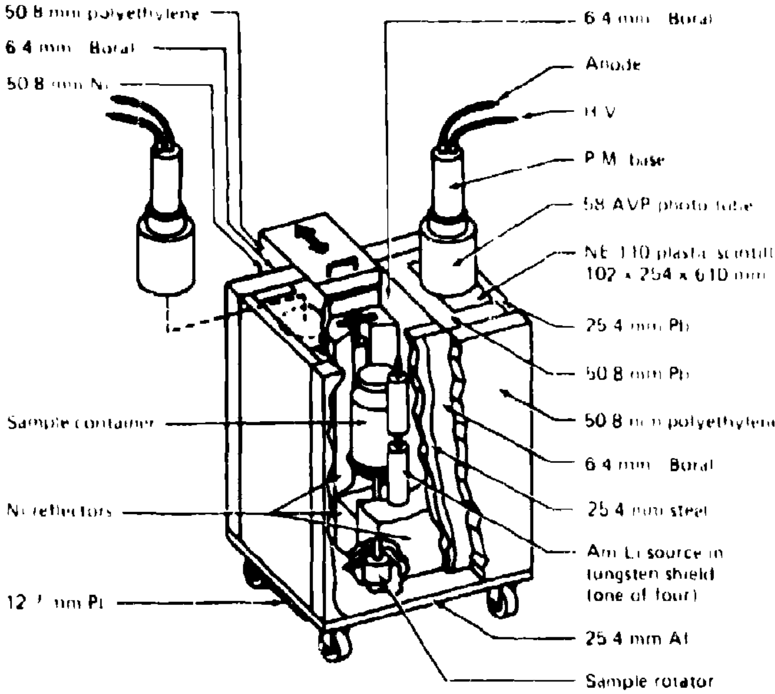

Figure 5.26 Cutaway view of Random Driver Mod-III. Not shown are the two ^{3}He proportional counters located along diagonal corners of the sample cavity. The Am-Li sources are not used for passive assay. (Ref. 81)

The amount of multiplication is relatively larger for samples with larger fissionable content and can lead to incorrect high assays. Also light element impurities (Li, Be, B, C, O, F, Na, Mg, Cl) can undergo (α,n) reactions, producing accidentals and neutron-induced fission. In the latter case, correlated neutrons and gamma rays that cannot be distinguished from those resulting from spontaneous fission events will result in a high assay.

The scintillator light output is relatively insensitive to temperature. The light output from the most commonly used scintillator, NE102 (manufactured by Nuclear Enterprises, 931 Terminal Way, San Carlos, Calif. 94070), is independent of temperature from −60°C to +20°C and decreases by 5% when the temperature is increased to 60°C. The drift caused by the temperature sensitivity of the PM may be a problem, however, unless the system is used in a temperature-controlled room.

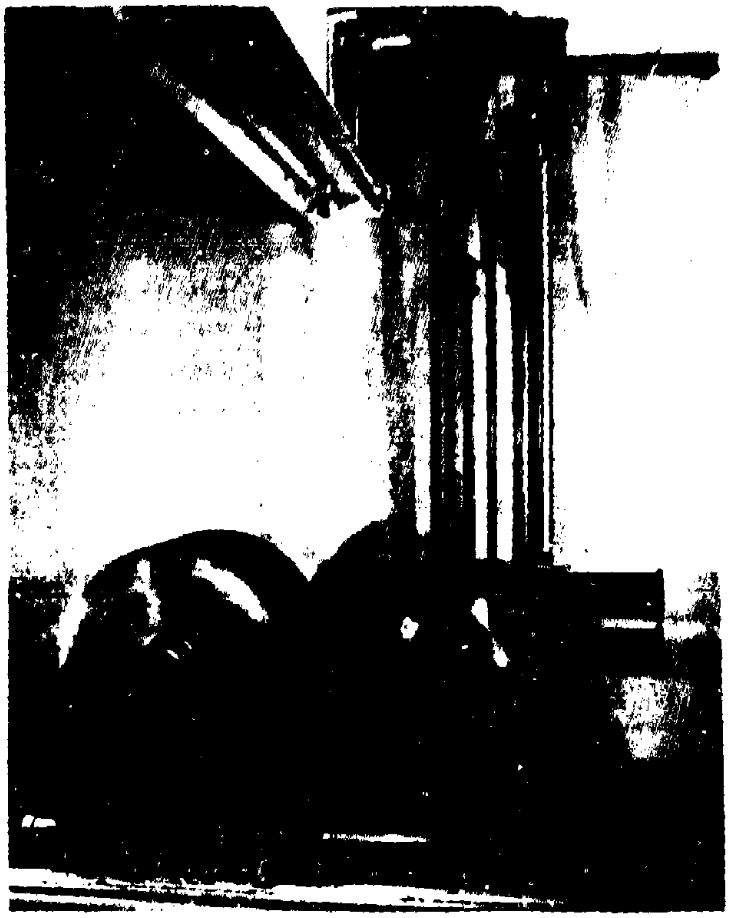

Figure 5.27 An Isotopic Source Assay System (ISAS). The cylindrical cask on the left is for storage of a ^{252}Cf neutron source when the system is in the active mode. The system has four large plastic scintillators, and a sample rotator and translator. A 10-L bottle is shown in the sample holder. (Photograph courtesy of IRT Corp.)

Measurement Control Requirements

For the most accurate measurements, the matrix variations of assay items should be controlled, especially moderator and high-Z materials and materials with high neutron absorbance cross sections (neutron poisons). Because of the wide variety of compositions typically measured and the sensitivity of this assay method to composition, traceable physical standards are not available. Separate standards covering the range of SNM mass to be assayed are needed for each of those material types where variation in material type is known to affect the assay significantly.

All these systems use PMs, and a normalization standard should be used at least daily to correct for PM drift with time. A 50-ng ^{252}Cf source may be used as a normalization source. Controlling the temperature of the room where the instrument is located will reduce the drift.

Data Analysis Requirements

The calibration of the system requires the measurement of a series of standards that span the SNM mass range of interest. If the response is linear and passes through the origin when plotting response as a function of SNM mass, then the calibration equation is

$$M = \mathrm{CR}\,K \qquad (5\text{-}40)$$

where M = grams of Pu; CR = counts per second for the sample; and K = grams per n count per second, the average slope from calibration sources.

Where the response is not linear, a least-squares fit of the appropriate functional form to the data is required. The amount of ^{240}Pu (and hence Pu) is determined by using the fitted calibration curve. For a Random Driver an equation relating the mass M to the count rate CR of the form

$$\mathrm{CR} = \frac{aM}{1 + bM} \qquad (5\text{-}41)$$

is used, where a and b are constants determined by a least-squares fitting procedure (Refs. 1 and 81).

Survey of Selected Literature

Metal Plates (Ref. 78)

The material assayed was 0.025-cm thick metal plates containing about 5 g of ^{240}Pu. The isotopic composition was 93.4% ^{239}Pu and 6.0% ^{240}Pu. A threefold coincidence was used with an Isotopic Source Adjustable

Fissiometer operated in an air-conditioned room. The response was linear from 0.5 to 5 g of ^{240}Pu.

PuO_2 Powder (Ref. 79)

The material assayed was PuO_2 powder. A threefold coincidence was required from a four-detector system, a Random Driver, that was designed for samples of small size. For an effective ^{240}Pu mass from 0.1 to 0.3 g, the response was linear. The system sensitivity was 10 mg of ^{240}Pu for a 10-min count.

Combustible Waste (Ref. 80)

The material assayed was ^{240}Pu in a 55-gal. drum filled with paper and cloth.

This system has ten 5-in. diameter by 60-in. long liquid scintillators arranged in a semicircle to accommodate a 55-gal. drum. A NaI detector was used as a diagnostic indicator for ^{239}Pu. A drum rotator was used. Coincidences up to 10 out of 10 were available.

With a coincidence requirement of 3 out of 10, two fuel-pellet standards were measured as 0.05 ± 0.01 g (1σ) and 0.41±0.01 g (1σ) ^{240}Pu in 2000-s measurements. The uncertainties quoted are from counting statistics only. In a 5-min count, 0.16 g of ^{240}Pu could be measured with a precision of 16% (1σ). The response was determined to be linear from 0.01 to 60 g of ^{240}Pu.

5.2.4 Alpha Counting: On-Line Alpha Measurements

Alpha radiation is used in determining both Pu and U content and isotopic abundances. The short range of alpha radiation (approximately tens of micrometers) requires chemical treatment of sample material to produce a thin sample suitable for alpha counting. If the specific activity (e.g., dis/s-g SNM) is known, then the alpha count rate can be used to measure SNM content. Isotopic abundance determination using alpha pulse-height spectroscopy is discussed in Section 4.8.2.

Although the most common use of alpha counting for assay involves measurement under well-controlled conditions, monitoring Pu concentrations in the harsh environment of a process line in a fuel reprocessing plant is possible, and this application is discussed in this section. The measurement of SNM concentrations including chemical methods is discussed in Section 4.9.6.

Description of Method

A measurement of the total number of alpha particles per unit time from a thin sample of SNM can be used to determine the amount of SNM present. This measurement can be used to monitor the amount of Pu solution flowing past a detector. The solution can contain fission products giving a high beta- and gamma-ray background. These solutions are part of the material in process lines at a fuel reprocessing plant. Thin detectors, either Ce-activated glass scintillators or Si surface-barrier detectors, can be used. The glass scintillators can be in direct contact with the Pu-bearing solutions, whereas a thin barrier is needed to isolate Si detectors from the process solution. Discrimination is needed against beta- and gamma-ray activity, which may be present at much higher intensities than the alpha activity. The beta particles, which have longer ranges, pass through the thin detector and deposit little energy in it, and thus produce pulses that are much smaller than those produced by alpha particles. The alpha intensity is measured by setting a lower level discriminator above the pulse heights caused by beta particle interactions. Although glass scintillators have poorer resolution than do the semiconductor detectors, they are much less sensitive to radiation, chemical, and mechanical damage.

Scope of Applications

Glass scintillators have been used to monitor waste streams in a Purex-type fuel-reprocessing-plant process that have Pu concentrations from 10^{-4} to 5 g/L.

Summary of Performance

A performance summary is given in Table 5.21.

Equipment

A cerium-activated glass scintillator detector is connected to a flow chamber that directs the liquid across the face of the scintillator. The flow chamber is located in a shielded cell and is connected to the process line by a sampling line. The thicknesses of solutions that are exposed to the detector range from about 0.1 to 0.5 mm, depending on the estimated sample stream activity. A photomultiplier, preamplifier, stable high-voltage supply, amplifier, SCA, and scaler-ratemeter are needed for the system. Preamplifiers and subsequent electronics may be located in a more accessible area with no degradation of performance. Through the use of additional electronics, process system alarms can be activated for count rates above or below set levels. A multichannel analyzer simplifies detector setup and calibration. A complete system including electronics costs $22,000.

A Si detector system would require a flow chamber with a protective barrier for the detector. The electronics required is similar to that required for a glass scintillator system except that a PM would not be needed.

Table 5.21 Summary of performance: on-line alpha measurements[a]

			Performance (% RSD)			
Sample Type	Concentration Range (g/L Pu)	Container	Random Error	Systematic Error	Remarks	Ref.
Pu nitrate solutions	10^{-4} to 1	Stainless steel and glass flow chamber	—	—	Linear response with concentrations	82
Pu nitrate solutions	10^{-4} to 3	Stainless steel and glass flow chamber	—	5	Insensitive to fission product activity	83

[a] All data from literature survey.

Major Sources of Error

Discriminator levels are set to eliminate beta-gamma interference; however, the increased count rate for high beta activity may contribute to the count rate if discriminator levels are set low enough. An increase in sensitivity was noted at the higher Pu concentrations (≈ 3 g/L) and may be the result of pulse pileup at the high counting rates observed (40,000 counts/s). Plutonium may also plate out on the detector or protective barrier, causing a time-dependent background. This will require a large background correction at low Pu concentrations. Nonuniformity in the fluid density and presence of other alpha particle emitters can also cause errors. Because the in-line monitor does not discriminate between alpha particles from the various isotopes, changes in isotopic composition can cause systematic errors in calibration. Wide variations in specific activity will result from different burnups (Ref. 83).

Measurement Control Requirements

The discriminator level is set using a beta source, such as ^{90}Sr, and an ^{241}Am alpha source. The discriminator level is set above the bulk of the beta energy spectrum at 20% to 30% of the alpha peak value. At the highest Pu concentrations (3 g/L) PM gain shifts of up to 10% may occur (Ref. 83), and this must be checked during the initial calibrations.

The system is calibrated by flowing solutions containing known concentrations of Pu through the counting chamber. The concentrations must cover the range of the sample concentrations. A least-squares fit can be made to the graph of the count rate as a function of concentration, which is linear over a wide range of Pu concentrations.

A check of system stability should be made regularly with a normalization source as well as a background count to check for Pu plating out.

Data Analysis Requirements

The relation of measured sample counts per second to Pu concentrations is made using a calibration curve (assuming no differences between the sample and calibration solutions). The same discriminator level must be used for the calibrations and samples. Nonlinear or piecewise linear calibration curves may be needed to describe the response curve at the highest concentrations.

Survey of Selected Literature

Plutonium Nitrate Solutions (Ref. 82)

Plutonium nitrate solutions containing 10^{-4} to 1 g/L of Pu were assayed. Concentrations were measured for process control purposes using in-line detectors.

A laboratory test loop was used to circulate Pu solutions with varying concentrations past a cerium-activated glass scintillator, 0.25 mm thick. The sample was 3.2 mm thick. At 10^{-4} g/L Pu, the count rate was 100 counts/min and at 1.0 g/L, 8.3×10^5 counts/min. The source chamber was made of polished stainless steel to aid in decontamination. A discriminator level of 20% of the alpha pulse height was used.

Tests with a Ra D-E-F beta source and a ^{137}Cs source showed that these sources of interference had no effect on response. A linear response to Pu concentration was found over the entire concentration range. Subsequent performance of this unit in a reprocessing plant sampler line was satisfactory.

Plutonium Nitrate Solutions (Ref. 83)

Acidic solutions containing 10^{-4} to 3 g/L of Pu spiked with varying amounts of ^{90}Sr were assayed. A cerium-activated glass scintillator system, an on-line alpha monitor, was used with a laboratory test loop circulating acidic solutions containing Pu solutions with concentrations of 10^{-4} to 3 g/L. Figure 5.28 is a photograph of an on-line alpha monitor. The stream, 0.28 mm thick, was used to mock up a process stream containing low burnup light-water-reactor (LWR) grade Pu. Discrimination

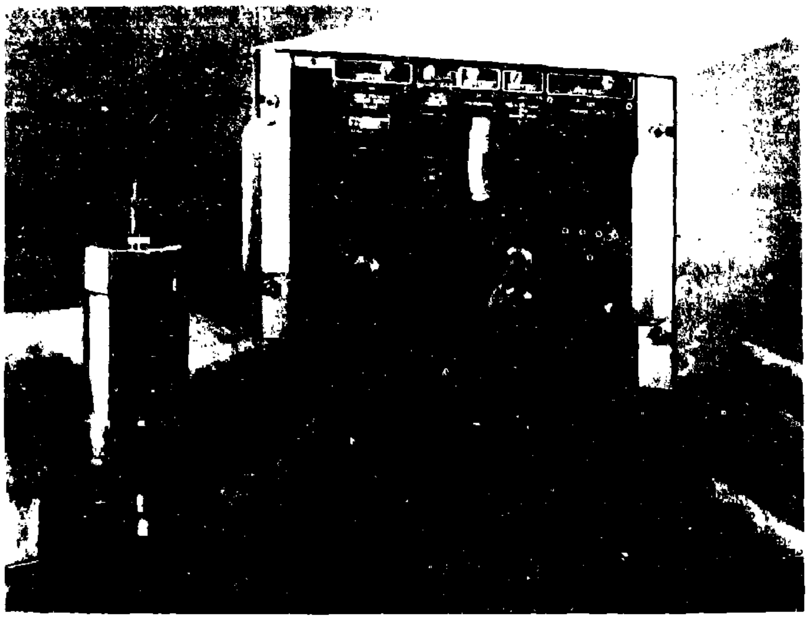

Figure 5.28 On-line alpha monitor. (Figure courtesy of IRT Corp.)

against beta particles was tested by adding ^{90}Sr to the solutions at concentrations 10^3 to 10^8 dis/min/mL.

With the discriminator set at 30% of the full energy alpha pulse height and for solutions with 0.01, 0.06, and 1.4 g/L Pu, the alpha particle count rate was independent of ^{90}Sr beta activity levels from 10^3 to 10^8 dis/min/mL. The alpha sensitivity was 52.0 ± 2.6 counts/s/μCi/mL for 10 standards with Pu concentrations ranging from 10^{-4} to 2 g/L. The uncertainty was calculated from the averages of over 500 10-s spectra taken automatically for each concentration.

5.2.5 Calorimetric Assay

Description of Method

A radiometric calorimeter is a device for measuring heat associated with the decay of radioactive materials. The radioactive decay of both U and Pu generates heat, but for SNM presently processed in large quantities, only Pu, because of its shorter half-life and hence higher specific activity, generates enough heat to be measured accurately. Most of the Pu decay energy is released as alpha or beta particles and converted to heat through absorption into the material. A small portion of the decay energy is carried away from the calorimeter by neutrons and gamma rays, but this energy is less than 0.01% of the total. Thus, calorimetric assay of Pu consists of a calorimeter measurement of the heat released through the radioactive decay of Pu and the determination of the proper analytical factor for converting the calorimetric measurement to mass of Pu.

The analytical factor for calorimetry is the effective specific power P_{eff} expressed in watts per gram of Pu. P_{eff} is a function of the specific power P_i and the relative amounts R_i of each of the Pu isotopes and ^{241}Am:

$$P_{eff} = \sum_i R_i P_i \qquad (5\text{–}42)$$

Recommended methods for calibrating calorimeters as well as for determining P_{eff} are detailed in ANSI N15.22-1975 (Ref. 84), which defines two methods for determining the effective specific power. The first, known as the empirical method, involves a microcalorimetry measurement and the chemical assay of a small aliquot of material. P_{eff} is defined as

$$P_{eff} = \frac{W}{\text{Pu}} \qquad (5\text{–}43)$$

where

W = measured thermal power of the aliquot, watts
Pu = total Pu content of the aliquot, grams

When the Pu concentration is too low for accurate chemical analysis or a totally nondestructive assay is required, the computational method may be used to determine P_{eff}. In this case the relative abundances of all the Pu isotopes and ^{241}Am are determined independently, and P_{eff} is computed from Eq. 5–42. Recommended values for P_i are provided by ANSI N15.22.

For the most accurate and precise determination of P_{eff} by the computational method, mass spectrometry, alpha pulse-height analysis, and/or high-resolution gamma-ray spectrometry of liquids may be used to determine the isotopic composition. High-resolution gamma-ray spectroscopy of solids may also be used to determine P_{eff} nondestructively.

Calorimetric assay offers several distinct advantages over chemical analysis and other nondestructive assay techniques: (1) the conversion factor remains the same (with correction for nuclear decay) as long as the isotopic composition is not changed: thus, the same factor is applicable to all Pu-bearing materials from a particular batch of PuO_2, including PuO_2, mixed oxides, and scrap; (2) the attribute measured (heat) is directly related to Pu content; (3) the power measurement is matrix independent because it is unaffected by variable self-attenuation of gamma and neutron radiation in the sample matrix; (4) calorimetry is highly accurate and precise; and (5) calorimetric assay is directly traceable to the national measurement system.

Some important limitations of the method are that the calorimeter cannot distinguish between heat produced by radioactive decay and heat produced by other sources, such as chemical reactions; and when it is applied to chemically inhomogeneous materials, accurate isotopic measurements are required.

Scope of Applications

Calorimetry has been applied to a wide variety of Pu-bearing solids including metals, alloys, oxides, fluorides, mixed U-Pu oxides, and waste and scrap (e.g., ash, ash heels, greencake, crucibles, and graphite scarfings). Because of its insensitivity to matrix effects, calorimetric assay of process materials is often used to provide calibration data for other NDA techniques (Ref. 85).

Instruments have been fabricated that are c[illegible] of accepting containers ranging in size from 1 to 30.5 cm in [illegible] 16 mL to 30 L in volume) and fuel rods up to 3 m long. The upper limit of the quantity of Pu that may be measured in a calorimeter is dictated only by nuclear safety considerations. For instruments used in production environments, detectability ranges from 0.01 to 0.2 g of Pu/L, depending on P_{eff} of the Pu and instrument sensitivity.

Summary of Performance

The accuracy and reliability of calorimetric assay is primarily dependent on the amount of Pu present and on the methods used to determine P_{eff}.

For materials with high Pu concentrations (e.g., metals, oxides, and alloys), random and systematic errors are comparable to good chemical assay techniques (Ref. 86). The reason for this is that at higher Pu concentrations (>100 g of Pu/L) power measurements with random and systematic errors of 0.1% or better are achievable. In addition, for high concentration materials, P_{eff} can be determined by the empirical method, which involves a direct comparison with chemical assay.

When the computational method is used to determine P_{eff}, systematic errors of 0.1% to 0.2% occur because of uncertainties in the specific powers recommended in ANSI N15.22. These are being remeasured with the goal of reducing these uncertainties to less than 0.1%. These measurements will be included in the next revision of ANSI N15.22.

For the most precise isotopic measurements, the random errors of the computational methods approach those of the empirical method. For example, when high-resolution gamma-ray spectroscopy of solutions is used, random errors of 0.1% to 0.6% (2σ) were achieved with a wide variety of isotopic compositions. Similarly, when high-precision mass spectrometry is combined with alpha pulse-height analysis for ^{238}Pu, random errors ranging from 0.1% to 0.5% were achieved. When mass spectrometry is also used for ^{238}Pu analysis, random errors ranged from 0.2% to 1.2%. In general, the precision of the ^{238}Pu analysis is often the determining factor in the size of the random error, because the specific power of ^{238}Pu is nearly 300 times that of ^{239}Pu. When the gamma-ray spectroscopy of solids is used, the uncertainties of the Pu assay range from 0.5% to 1.5%.

Analysis time depends on the calorimeter, the sample size, and the method used to determine P_{eff}. For small samples (e.g., in 10-mL vials) calorimeter measurement time varies from 15 min to 1 h. For process samples (e.g., in 11-cm diameter tin cans) calorimeter measurement time varies from 4 to 16 h. The shorter times are achieved by using prediction of equilibrium and/or servo-control techniques to speed up the measurement. The time to complete a P_{eff} determination depends on the technique used: the empirical or computational method. Counting time for the gamma-ray spectroscopy measurement varies from 15 min to 16 h for solutions, and from 4 to 16 h for solids.

Because of the nature of this technique, the summary table (Tables 5.22 and 5.23), is separated into two parts, performance of heat

Table 5.22 Summary of performance: heat measurements

Material	Container (Diameter by length, cm)	Quantities (g Pu)	P_{eff} (mW/g Pu)	Assay Time (h)	Performance (% RSD) Random Error (% RSD)	Performance (% RSD) Systematic Error (% RSD)	Source[a]	Ref.
PuO_2	404 tin can, 10.8-cm diameter	600	2.4	8	0.10	0.09	E	
				8	0.03	0.03	L	86
				8	0.04	0.04		
				24	0.17	0.13		
	404 tin can	1000	5.1	3 to 8	0.03	—	L	86, 87
			3.1		0.03			
			5.0	8	0.02	—	L	86, 88
			3.0	8	0.02	—		
PuO_2, Pu Metal	404 tin can	200 to 2200	2.4 to 10	8	0.04	0.03	U	
Pu in polystyrene blocks	—	40 to 200	2.4	8	0.08	0.03	U	
Pu metal, PuO_2	404 tin can	2200	2.4	24	0.2	—		

Note—See footnote at end of table

Table 5.22 Summary of performance: heat measurements (Cont'd)

Material	Container (Diameter by length, cm)	Quantities (g Pu)	P_{eff} (mW/g Pu)	Assay Time (h)	Performance (% RSD) Random Error (% RSD)	Performance (% RSD) Systematic Error (% RSD)	Source[a]	Ref.
PuO_2 hard scrap	Gallon can	50 to 500	2.4	12	0.25	0.05	U	
				12	0.5	0.08		
				16	0.75	0.25		
	12 by 25	10 to 200	2.4	8	0.08 to 0.6	0.1 to 0.5	U	
		40 to 200	2.4	8	0.27	0.09		
PuO_2, Pu metal, MOX	2.8 by 7.6	6 to 60	2.4	2.5	0.5	0.2	U	
				2.5	0.3	0.1		
	1.5 by 5.0	4 to 20	2.4	1	0.05	0.04	U	
PuO_2, Pu metal	2.0 by 6.0	4 to 20	2.4	0.5	0.25	0.10	U	
MOX	1 by 90 fuel pin	50 to 200	3.0	0.5	0.2	—	L	86, 89
$^{238}PuO_2$	16.5 by 30.5	100 to 200	450	1.5	0.10	0.04	U	
					0.14	0.05	U	

[a]E = survey of exchange programs; L = literature survey; U = users' survey of production facilities.

Table 5.23 Summary of performance: effective specific power measurements

				Performance (% RSD)			
Material	**Method**	**Isotopic Composition (% ^{240}Pu)**	**Assay Time(h)**	**Random Error (% RSD)**	**Systematic Error (% RSD)**	**Source[a]**	**Ref.**
PuO_2, MOX and Pu metal	Empirical: 100 g Pu/L	70 to 94	—	0.04 to 0.09	0.06	L/E	86
		All		Range: 0.04 to 0.55	Range: 0.1 to 0.4	L/E	86
				Average: 0.33	Average: 0.11		86, 89
	Computational: mass spectrometry	94 (NBS-948)	—	Range: 0.15 to 0.55	Interlaboratory bias:	L/E	86, 89
				Average: 0.33	0.1 to 1.1		
					Average: 0.5		
		84 (NBS-946)	—	Range: 0.13 to 0.60	Interlaboratory bias:	L/E	
				Average: 0.35	0.3 to 2.0		
					Average: 0.6		
		86 (JK-131)	—	Range: 0.15 to 0.42	Interlaboratory bias:	L/E	
				Average: 0.24	0.2 to 1.0		
					Average: 0.6		
		86	—	0.14 to 0.36	0.07	L	
		76	—	0.10 to 0.12	0.06 to 0.11	L	(b)
		70	—	0.13 to 0.20	0.06 to 0.08	L	(b)
	Mass spectrometry (Alpha Pulse-Height analysis for ^{238}Pu)	94	—	0.09	<0.2	L	86, 90
		86	—	0.06 to 0.29	0.06 to 0.09	L	[illegible], 90
		76	—	0.05 to 0.34	0.06 to 0.10	L	(b)
		70	—	0.08 to 1.1	0.06 to 0.30	L	(b)

Note—See footnote at end of table.

Table 5.23 Summary of performance: effective specific power measurements (Cont'd)

Material	Method	Isotopic Composition (% ^{239}Pu)	Assay Time (h)	Performance (% RSD)		Source[a]	Ref
				Random Error (% RSD)	Systematic Error (% RSD)		
	Gamma-ray spectroscopy of solutions (plus isotopic correlation for ^{242}Pu [Ref. 96])	94	—	0.1	—	L	86, 91
		90	—	0.2	—	L	86, 91
		86	16	0.08	0.06	L	86, 91
		76	22	0.20	0.08	L	(b)
		70	20	0.08	0.06	L	(b)
		76	—	0.17	—	L	92
		70	—	0.32	—	L	92
Low density (ash)	**Gamma-ray spectroscopy of solids (plus isotopic correlation for ^{242}Pu [Ref. 96])**	72 to 98	2.8	1.2	0.4	L	86
High density		72 to 98	5.5	1.2	0.4	L	86
Low density		98	2.8	3.6	1.1	U	
		91 to 93	2.8	0.85	0.10	U	
High density		86 to 91	5.5	0.91	0.24	U	
Low density		80 to 86	2.8	1.6	0.50	U	
		70 to 76	2.8	1.3	0.33	U	
Low density (Am = 1%)		85	2.8	1.3	0.20	U	
Low density (Am = 0.06%)		86	2.8	0.83	0.14	U	

Note—See footnote at end of table.

Table 5.23 Summary of performance: effective specific power measurements (Cont'd)

Material	Method	Isotopic Composition (% ^{239}Pu)	Assay Time(h)	Performance (% RSD) Random Error (% RSD)	Systematic Error (% RSD)	Source[a]	Ref.
Oxides, metals Sulfates	Two detectors	71 to 93	13.3	1.0	—	L	93
Oxides		93	2 to 10	0.1 to 0.2	—	L	86, 94
Fast Flux Test Facility fuel	**Stream averages**	—	—	2.35	—	L	95
	Stream average plus[b] ^{238}Pu and ^{241}Am by gamma-ray analysis	—	—	0.65	—	L	95

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[a] E = survey of exchange programs; L = literature survey; U = users' survey of production facilities.

[b] D. R. Rogers, W. W. Rodenburg, R. J. Seiler, and R. L. Goss, "Experimental Evaluation of Calibration Alternatives for Calorimetric Assay of Reactor-Grade PuO_2." (MRC-Mound Report, in preparation.)

measurements and performance of effective specific power measurements. The overall uncertainty in grams of Pu can be estimated by combining error variances for the two components of the assay (Eqs. 5–48 and 5–49). Some results are summarized in Table 5.24.

Equipment

Power Measurement

Although many calorimeter designs have been developed, the most successful ones all fit the general category of heat flow calorimeters. A heat flow calorimeter consists of a sample chamber thermally insulated from a constant temperature environment by a thermal gradient (Fig. 5.29).

When a Pu sample is placed in the sample chamber, the temperature rises or falls until the heat lost through the thermal gradient equals the heat produced by the sample:

$$W_S = \frac{T_S}{R_{\text{th}}} \qquad (5\text{–}44)$$

where

W_S = thermal power of sample, W
T_S = temperature rise caused by sample, °C
R_{th} = thermal resistance of calorimeter, °C/W

Thus the temperature rise in the calorimeter is proportional to the power of the sample, and the R_{th} is the proportionality constant:

$$T_S = R_{\text{th}} W_S \qquad (5\text{–}45)$$

Calibration is by means of electrical heat or physical heat standards prepared from $^{238}\text{PuO}_2$:

$$R_{\text{th}} = \frac{T_{\text{std}}}{W_{\text{std}}} \qquad (5\text{–}46)$$

where

W_{std} = thermal power of standard, W
T_{std} = temperature rise caused by standard, °C

A potentiometer or a digital voltmeter capable of resolving microvolt level signals is typically required for readout of the various electrical signals.

Table 5.24 Summary of performance: calorimetric assay

Material	$P_{\rm eff}$ Determination	Performance (% RSD)		Source[a]
		Random Error	Systematic Error	
Oxides, MOX, and metal in 404 tin can, 200 to 2200 g Pu	Chemical analysis	0.05 to 0.59 Average: 0.17	0.07 to 0.42 Average: 0.22	L
	Mass spectrometry	0.13 to 0.63 Average: 0.3	0.07 to 2.0 Average: 0.5 (interlaboratory bias)	U/E
	Mass spectrometry and alpha pulse-height analysis	0.06 to 1.1 Average: 0.4	0.07 to 0.33 Average: 0.15	L
	Gamma-ray spectroscopy of solutions and isotopic correlation	0.09 to 0.36	0.08	L
	Gamma-ray spectroscopy of solids and isotopic correlation	0.1 to 1.5	0.1 to 0.5	L/U
Pu scrap in 1-gal. containers:				
50 to 500 g Pu	Mass spectrometry	0.28 to 1.0	0.1 to 0.65	L/U
	Mass spectrometry and alpha pulse-height analysis	0.25 to 1.3	0.08 to 0.39	U
20 to 1200 g Pu	Gamma-ray spectroscopy of solutions	0.09 to 0.36	0.08	L
	Gamma-ray spectroscopy of solids	0.9 to 3.6	0.10 to 1.1	U

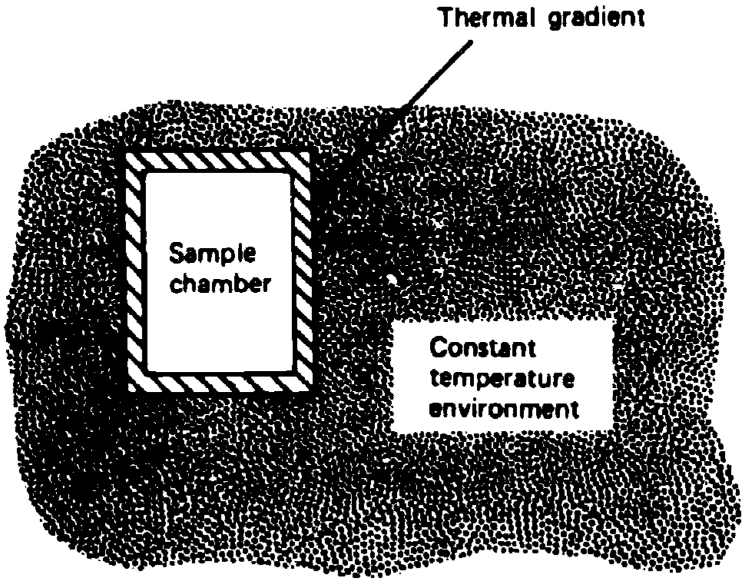

Figure 5.29 Heat flow calorimeter schematic.

The approach to equilibrium is a function of several exponentials with different time constants related to the specific heat and thermal conductivities of such elements as the source, the container, the calorimeter chamber, and the thermal gradient media. The temperature difference is sampled periodically or monitored on a recorder until the temperature variation is sufficiently small to meet the desired accuracy.

Because calorimetry essentially involves a temperature measurement, it is often sensitive to variations in room temperature. Thus, a temperature-regulated metal block, several concentric zones of increasingly precise temperature control, or a water bath controlled to ±0.001 °C is used to provide a stable reference temperature for the calorimeter.

A twin unit thermally and physically identical to the sample unit is also often used to increase the signal-to-noise ratio and to improve the instrument stability.

The instruments are not readily available commercially but have been produced by several Department of Energy (DOE) Laboratories, and drawings are available. Costs are expected to range from $25,000 to $80,000 each depending on sample size, precision, time per assay, and degree of automation required.

Effective Specific Power Determinations

For the empirical method, a microcalorimeter and Pu analysis capability are required. Several microcalorimeters with precisions of ±0.10% at the 10 mW level have been developed. (Plutonium assay is discussed in Section 4.9.) For the computational method ^{241}Am and Pu isotopic analysis capabilities are required.

Major Sources of Error

The most important limitation of the method is that the calorimeter cannot distinguish between heat produced by radioactive decay and heat from other sources such as chemical reactions.

Interferences from chemical reactions are generally minimized by the use of hermetically sealed containers and by confining the method to dry solids. Calorimetry cannot be recommended for Pu-bearing solutions until further data are available on the kinetics and thermodynamics of the specific systems. Interferences from chemical reactions or other heat-producing isotopes can be detected by (1) observation of the time dependence of the calorimeter measurement to detect chemical reactions, (2) gamma-ray spectrometry to detect fission-product contamination, (3) comparison of the Pu assay with an assay by an independent technique, and (4) process control information.

Measurement Control Requirements

Standards Available

For calorimeter calibration there are two types of standards available, both traceable to NBS. Either an electrical heater or a heat standard containing certified amounts of ^{238}Pu may be used. In general, the physical standards are preferred because they provide a calibration of the total system. Heat standards ranging from 2 mW to 40 W have been fabricated.

For calibration of coulometers, mass spectrometers, etc., NBS-certified Pu isotopic and assay standards are available. (See appropriate sections of this handbook for more details about specific instruments.)

Calibration/Certification/Verification

Maintaining adequate measurement assurance for the power measurement is relatively easy. The ^{238}Pu-fueled heat standards are measured first to establish an initial calibration, and then are measured periodically thereafter to provide assurance that the initial calibration is still valid. Frequency of measuring standards varies from daily to monthly. The longer frequencies are generally associated with scrap measurements in which the calorimeter variability is very small compared to the variability of the P_{eff} determination. A typical measurement assurance plan along with numerical examples may be found in Reference 95. Measurement assurance programs for the various components of the P_{eff} determination should also be applied.

Data Analysis Requirements

Data Requirements

To calorimetrically assay for Pu the following information is required:

W_S = sample power, W
R_i = mass ratios of ^{241}Am and all Pu isotopes, g/g of Pu
T_1 = date of calorimeter measurement
T_2 = date of Pu isotopic measurements
T_3 = date of ^{241}Am measurements

If the empirical method is used, the following additional information is required:

Pu = Pu content of analytical aliquot
W_A = power of analytical aliquot, W

Computation

Given the data listed in the preceding paragraph, each of the isotopic ratios is first decayed to the date of the calorimeter measurement. The ratios are then normalized so that the sum of the Pu weight fractions equals 1 and P_{eff} is calculated from Eq. 5–42. The quantity of Pu, G_{Pu}, is determined by dividing the power of the sample W_S by P_{eff} (determined by the computational or empirical method):

$$G_{Pu} = \frac{W_S}{P_{eff}} \tag{5-47}$$

The uncertainty of the analysis is estimated from the uncertainty in the individual components. For example, when the empirical method is used,

$$S^2(G_{Pu}) = S^2(W_S) + S^2(W_A) + S^2(\mathrm{Pu}) \tag{5-48}$$

where S^2 is the relative error variance of the variable in the parentheses.

If the computational method is used, the error estimate includes uncertainties in the power measurement, the isotopic measurements, and the specific powers of the various isotopes P_i:

$$S^2(G_{Pu}) = S^2(W_S) + \sum_i \left[\frac{R_i P_i}{P_{eff}}\right]^2 [S^2(R_i) + S^2(P_i)] \tag{5-49}$$

For details of the calculation and error estimates, see References 84 and 95.

Survey of Selected Literature

Plutonium Bearing Feed Materials (Ref. 86)

Materials with high Pu concentration, such as PuO_2, Pu metal, and MOX were assayed. A recent study completed in 1977 evaluated the reliability of calorimetric assay for use in shipper-receiver measurements. The estimates are given in Table 5.25.

Plutonium Metal and Oxide (Refs. 90 and 97)

PuO_2 and Pu metal of four different isotopic compositions ranging from 70% to 93% ^{239}Pu were assayed.

Mass spectrometry and alpha pulse-height analysis for ^{238}Pu were performed. In addition P_{eff} was determined by the empirical method for comparison purposes. As expected, the ^{238}Pu measurement was the largest source of error because of its high specific power. (See Table 5.26.)

Plutonium Bearing Solids (Ref. 97)

Bulk quantities of Pu-bearing solids containing more than 400 g of Pu were assayed. Measurements were made with a transportable calorimeter designed for (DOE) auditors and with a high-resolution gamma-ray-spectroscopy system. The calorimeter was designed with a minimum amount of material that would attenuate gamma rays so that the calorimetry and gamma-ray measurements could be done simultaneously. The calorimeter precisions were 0.3% for samples containing more than 400 g of Pu. When combined with the gamma-ray measurements, the precision of the Pu determination was 1.0% for overnight runs and 1.2% for 4-h measurements.

Plutonium Metal Exchange Samples (Refs. 86 and 89)

Plutonium isotopic exchange samples were assayed. P_{eff} was calculated from mass spectrometry and/or alpha spectrometry isotopic abundance data. The measurements were made as part of the metal exchange program. Each laboratory reported results of isotopic analysis of three samples: two NBS standards (NBS–946 and NBS–948) and UK–131. Results for 1976 were used.

Average random errors ranged from 0.2% to 0.4% for the three isotopic compositions. (See Table 5.27.) Average systematic errors based on intersite bias ranged from 0.5% to 0.76%.

Table 5.25 Summary of performance: reliability of calorimetric assay for shipper/receiver measurements on plutonium

Case	Method	Random Error (% RSD, 2σ) Range	Random Error (% RSD, 2σ) Average	Systematic Error (% RSD, 2σ) Range	Systematic Error (% RSD, 2σ) Average
1	Calorimetry alone (watts exchange)	0.03 to 0.37	0.17	0.023 to 0.14	0.07
2	Calorimetry plus P_{eff} (empirical)	0.07 to 1.1	0.33	0.10 to 0.40	0.22
3	Calorimetry plus P_{eff} (computational) using alpha or mass spectrometry or both	0.15 to 1.1	0.62	0.11 to 0.61	0.31
4	Calorimetry plus P_{eff} (computational) using gamma-ray spectroscopy of liquids	0.12 to 1.1	0.43	0.11 to 0.58	0.27
5	Calorimetry plus F_{eff} (computational) using gamma-ray spectroscopy of solids	0.25 to 3.0	1.5	0.13 to 1.0	0.52

Table 5.26 P_{eff} using alpha pulse-height analysis or mass spectrometry or both

Laboratory	% ^{239}Pu	Random Error (% RSD)	Systematic Error (% RSD)	Bias from Empirical Method
		Alpha pulse-height analysis for ^{238}Pu and mass spectrometry		
1	94	0.07	0.06	0.17
1	93	0.10	0.06	0.25
1	86	0.06	0.06	0.11
1	73	0.05	0.06	0.21
1	70	0.08	0.06	0.07
2	86	0.29	0.09	0.17
2	73	0.34	0.10	0.63
2	70	1.15	0.30	1.90
		Mass spectrometry alone		
1	86	0.14	0.07	0.07
1	73	0.12	0.06	0.02
1	70	0.20	0.08	0.62
2	86	0.72	0.07	−0.31
2	73	0.20	0.12	0.12
2	70	0.26	0.06	0.10

PuO_2 Samples (Ref. 89)

Low-burnup PuO_2 in no. 404 cans (10.8 cm in diameter) were assayed. Four samples, 600 g each (1.4 W), were distributed to four different DOE sites. Each site performed calorimetric measurements, and three of the four sites performed destructive isotopic measurements (mass spectrometry and alpha pulse-height analysis).

Relative standard deviations of power measurements for the four laboratories were 0.08%, 0.14%, 0.02%, and 0.03%. Biases of the four laboratories from the exchange mean of the power measurements were +0.04%, +0.02%, +0.01%, and −0.07%. The biases of the P_{eff} measurement from the interlaboratory mean were −0.10%.

Soluble Plutonium-Bearing Materials (Refs. 86, 92, and 97)

Plutonium-bearing materials that will dissolve completely were assayed. Gamma-ray spectroscopy of liquid samples provides a simple yet effective technique for determining P_{eff}. Gunnink of the Lawrence Livermore National Laboratory (LLNL) has estimated random errors of 0.2% to 0.4% for Pu compositions ranging from 40% to 93% ^{239}Pu. Based on measurements made at LLNL, Allied-Gulf Nuclear Services, and the Savannah River Plant, these estimates have been verified for isotopic compositions ranging from 70% to 94% ^{239}Pu (See Table 5.28). Because ^{242}Pu has no useful characteristic gamma rays, it cannot be measured by this

Table 5.27 Summary of performance: P_{eff} computed from metal exchange results[a]

		Random Error (%)			Intersite Bias (%)			
Sample	^{239}Pu Content (%)	Minimum	Maximum	Average	Minimum	Maximum	Average	No. of Laboratories
UK-131	80	0.15	0.45	0.22	0.14	0.98	0.5	5
NBS-946	84	0.14	0.60	0.36	0.35	2.0	0.76	5
NBS-948	93	0.15	0.53	0.34	0.05	1.1	0.58	4

[a] Department of Energy program to compare Pu measurements at various DOE contractor facilities.

Table 5.28 P_{eff} performance: gamma-ray spectroscopy of liquids

^{239}Pu Content (%)	Relative Precision (%)	Ref.
93	0.10	88
90	0.23	88
87	0.07	87
78	0.18	
74	0.14	87
70	0.31	

technique. It must either be estimated from stream average values, determined by mass spectrometry, or by using isotopic correlation techniques (Ref. 96).

Various Plutonium-Bearing Materials (Ref. 86)

Plutonium oxide, ash, metals, polystyrene cubes, and miscellaneous scrap were assayed. The ^{240}Pu content ranged from 2% to 24%.

P_{eff} was determined by gamma-ray isotopic measurements of solids. For high-density materials, such as metals, a 20,000-s count with a count rate of 2000 counts/s was used. For low-density materials such as ash, a 10,000-s count at 3000 counts/s was used.

The precision based on replicate measurements ranged from 0.5% to 1.0% RSD, and the power measurement had a precision of 0.05% RSD. The measurement is biased 3.3% low for low burnup Pu and 4.8% high for the highest burnups. Linear regression analysis of the bias yields a line with zero bias at 91% ^{239}Pu and a slope of $-0.237\%/\%$ ^{239}Pu. The systematic error as a result of the uncertainty of this line is 0.4% at 91% ^{239}Pu.

Plutonium-238 (Ref. 86)

The material assayed was $^{238}PuO_2$ shipments, 170 g per container, measured at two laboratories. Both laboratories used similar water-bath type calorimeters. Each container generated approximately 100 W of power. The effective specific power constant was computed from mass spectrometry measurements.

Average intersite bias was 0.03% over a period of 2 yr. The precision of the instruments at two laboratories was 0.1% and 0.3% RSD. P_{eff} was calculated as watts per gram of ^{238}Pu since ^{238}Pu is the accountable material. Since 99.9% of the heat is produced by ^{238}Pu, the uncertainty in P_{eff} was very small (<0.02%).

5.3 URANIUM AND PLUTONIUM ISOTOPIC COMPOSITION

Isotopic composition determinations of SNM for accountability purposes are generally performed using mass spectrometry. This method provides the most accurate results but requires expensive equipment and a relatively long time before an assay result is available. Passive nondestructive techniques can be used to verify isotopic abundances of entire inventories of material where adequate sampling and mass spectrometric analysis would be too expensive and time consuming. The passive NDA methods that are employed include low-resolution (NaI) and high-resolution (Ge) gamma-ray spectroscopy and neutron counting.

Under certain conditions the measured intensity of a gamma-ray line from one isotope can be used to determine the abundance of that isotope. This application is discussed in Section 5.3.1.1 Measurement of the gamma-ray activity of known masses of pure U and Pu solutions for isotopic determinations is discussed in Section 5.3.1.3. Most isotopes of U and Pu or their daughter products emit gamma rays such that the measured ratios of gamma-ray intensities can yield information about the relative abundances of isotopes. Gamma-ray ratio methods for isotopic abundances are considered in Section 5.3.1.2. Passive neutron measurement of enrichments is discussed in Section 5.3.2.

Alpha counting of thin, specially prepared samples is used as an adjunct to mass spectrometry for ^{238}Pu determinations. This application is described in Chapter 4, Subsection 4.8.2.

5.3.1 Gamma-Ray Spectroscopy

Three passive gamma-ray techniques are used for SNM isotopic determinations: the enrichment meter, gamma-ray ratio, and direct measurement methods. In practice, the enrichment meter has been used mainly for verification of U enrichments; the gamma-ray ratio method has been used mainly for determination of Pu isotopic compositions; and direct measurement of specific gamma rays has been used for determination of the isotopic composition of Pu and U in solutions.

5.3.1.1 Enrichment Meter

Description of Method

Characteristic gamma rays, which come from a particular isotope of SNM in a sample and which are attenuated mainly by the SNM (self-attenuation) as they pass out of the sample, can be used to determine the amount of the isotope present. If the item is at least as thick as several mean free paths for the characteristic gamma ray, the "enrichment meter" principle applies, and the gamma-ray intensity is directly proportional to the relative amount of the isotope present. For U, ^{235}U enrichment can be determined, and for Pu, the isotopic fractions of several isotopes can be established. For the 186-keV gamma ray from ^{235}U, the mean free path in U is less than 0.4 mm, so a "thick" sample can actually be quite thin physically. Augustson and Reilly (Ref. 3); Bishop, Kurtz, and Wieczorek (Ref. 60); and Kull and Ginaven (Ref. 98) give details of the theory of the enrichment meter principle; therefore only a brief description will be given here.

If a collimated detector views a U-plus-matrix sample, the count rate CR of the detector is given (Ref. 3) by

$$\mathrm{CR} = I\Gamma\varepsilon A\varrho_U\int_0^\infty \exp\left[-(\mu_U\varrho_U + \mu_m\varrho_m)x\right]dx \tag{5-50}$$

where

I = isotopic enrichment
Γ = specific activity of the characteristic gamma ray, gamma rays/s $\cdot$ g ^{235}U
ε = total detection efficiency, including container absorption
A = area of the sample viewed, cm^2
ϱ = density, g/cm^3 (subscripts U and m refer to uranium and matrix)
μ = mass attenuation coefficient, cm^2/g
x = distance (within sample) to front edge of sample, cm

The integral can be evaluated to give

$$\mathrm{CR} = \frac{KI}{1 + \mu_m\varrho_m/\mu_U\varrho_U} \tag{5-51}$$

where $K = \Gamma\varepsilon A/\mu_U$ is a constant. If $\mu_m\varrho_m/\mu_U\varrho_U \leqslant 0.1$, the denominator in Eq. 5–51 is approximately 1, then the count rate is proportional to enrichment to 10% or better. For ^{235}U enrichment assay in a low-Z matrix material ($Z_m \leqslant 30$), using the 186-keV gamma ray, $\mu_m/\mu_U \approx 0.1$ and $\mu_m\varrho_m/\mu_U\varrho_U \leqslant 0.1$, if $\varrho_m/\varrho_U \leqslant 1$. If a calibration is performed with standards having the same chemical composition as the assay item but varying in enrichment, the denominator can be neglected.

For U in a form meeting the enrichment meter requirement, the measurement of the 186-keV gamma ray from ^{235}U yields the enrichment of the sample after calibration with standards of known enrichments. A NaI detector can be used for this measurement. Plutonium isotopic ratios can be determined by measuring characteristic gamma rays from the various isotopes using Ge detectors. The contributions from ^{238}Pu, ^{239}Pu, ^{240}Pu, and ^{241}Pu can be measured, but there are no useful gamma rays from ^{242}Pu.

For MOX fuel the Pu mass fraction $\varrho_{Pu}/(\varrho_{Pu} + \varrho_U)$ can be determined by an enrichment meter measurement of gamma rays. The measured count rate CR is related to the mass fraction E by

$$\mathrm{CR} = KFIE \tag{5-52}$$

where

K = calibration constant, $\Gamma \varepsilon A/\mu_{Pu}$

$$F \cong \left[1 - \frac{\varrho_U(\mu_{Pu} - \mu_U)}{(\varrho_U + \varrho_{Pu})\mu_{Pu}} + \frac{32}{239}\,\frac{\mu_O}{\mu_{Pu}}\right]^{-1}$$

Typically $F \approx 1.0$ and is constant with E over a limited range of E; μ_O is the mass absorption coefficient of oxygen. If the Pu mass fraction E is known, the isotopic enrichment I can be determined using Eq. 5-52. (Refs. 99 and 100.)

Scope of Applications

This method has found its principal application in surveys of large numbers of UF_6 cylinders and containers of low-enriched UO_2 powder. The measurements are used to verify the "tag" values. The method is limited to thick homogeneous samples such as metal, oxide, pellets, and UF_6. The measurements can be made at all enrichment levels.

Summary of Performance

See Table 5.29 for a performance summary.

Equipment

Enrichment measurements can be made with NaI detectors for U and Ge detectors for Pu and mixed oxides. The NaI systems require a detector, photomultiplier, preamplifier, amplifier, stable power supply and two single-channel analyzers. The Ge(Li) systems have a detector, preamplifier, amplifier, stable power supply, A/D converter, and a multichannel analyzer or small computer. A portable commercially available NaI system is shown in Figure 5.30. The electronics package is called a stabilized assay meter (SAM). A small ^{241}Am source is attached to the NaI crystal, and the constant amplitude pulse from ^{241}Am alpha decay is used to stabilize the instrument against drift. This system costs about $3300. Although a Ge system is not required for the U measurements, its use can simplify the background subtraction. Germanium systems cost from $15,000 to $25,000, depending on the complexity of the system.

Table 5.29 Summary of performance: enrichment measurements[a]

Sample Type	Isotopic Composition	Container	Container Volume (L)	Performance (% RSD) Random Error	Performance (% RSD) $\frac{\text{NDA}-\text{TAG}}{\text{TAG}}$	Performance (% RSD) Average $\frac{\text{NDA}-\text{TAG}}{\text{TAG}}$	Remarks	Ref.
UF_6 (solid)	1.3% to 3.1% ^{235}U	30A and 30B cylinders	763	—	5.3	0.3	Thickness measurement required	101
UF_6 (solid)	3.1% to 97.7% ^{235}U	5A cylinders	8	—	3.2, 3.4	−0.8, 0.9	Thickness measurement required	101,102
UO_2 powder	0.2% to 4.4% ^{235}U	Bucket	18.9	< 0.6	—	—		103
U metal	93% ^{235}U	—	—	—	1.9	0.7		102
U_3O_8 incinerator ash (80% U_3O_8)	1% to 20% ^{235}U	Can	8	<1	—	—	Detection of enrichment stratification. Ge(Li) detector.	104
UO_2, PuO_2 MOX pellets (1.6% to 9% Pu)	—	—	—	0.3 to 0.4	—	−0.6	Performance for estimated Pu mass fraction (based on 3 samples)	99
UO_2, PuO_2 MOX powders (2% to 17% Pu)	70% to 87% ^{239}Pu	Bottle in sealed can	0.5 to 1.0	^{238}Pu, 1.6 ^{239}Pu, 0.3 ^{240}Pu, 4.3 ^{241}Pu, 0.3	— — — —	— — — —		100

[a] All data from literature survey.

Figure 5.30 NaI detector, photomultiplier, and SAM-II unit. (Photograph courtesy of Eberline Instrument Corp.)

Systems based on high-purity Ge detectors can be portable, but there must be liquid nitrogen for Ge detector cooling at the place of use. An ultrasonic thickness gauge is needed to measure UF_6 cylinder wall thicknesses.

Sources of Error

Details about the causes of errors in enrichment meter measurements given by Bishop, Kurtz, and Wieczorek (Ref. 60) and Kull and Ginaven (Ref. 98) are summarized here. The material must be "thick" for the method to be applicable; that is, several mean free paths for the characteristic gamma ray. The material must be homogeneous because this method generally samples a thin layer at the surface. If the standards are different in chemical composition from the assayed items, the relative density $\varrho_m \mu_m / \varrho_s \mu_s < 0.1$, where s denotes SNM, must hold. The assay will be accurate to 10% or better in the latter case.

The gamma-ray detector must be collimated to view only the material to be assayed, and the material must have no voids in the area viewed. The material viewed must be a good representation of the material in bulk. Stratification in incinerator oxides leading to enrichment variations has been observed.

A correction for the container wall thickness must be made if the standard container is not the same as the sample container, since wall thickness variations can also cause errors. In the enrichment assay of UF_6 cylinders, errors can be caused by wall-thickness variations, Pa plate-out on cylinder walls (with a resulting change in the gamma background), and the presence of "heels." Freshly separated U from a reprocessing plant can contain ^{237}U (half life = 6.75 days), which has a 208-keV gamma ray that can overlap the 185.72-keV gamma ray from ^{235}U when NaI detectors are used.

Measurement Control Requirements

The standards for the enrichment calibration should be the same in chemical form and container type as the material being measured. For calibration, three or more standards of different isotopic composition spanning expected values should be used. A straight-line fit using a weighted least-squares technique should be made to establish the count rate as a function of enrichment. Mass spectrometry using certified standard reference materials is usually used to determine the isotopic composition of in-house standards.

For the measurement of ^{235}U using NaI systems with two SCAs, analyzers, one window is set around the 185.72-keV ^{235}U peak, and the other is set above it to measure the background. Standards and samples should be similar in age because the background depends on the 767-keV and 1001-keV gamma rays from ^{234m}Pa. During chemical processing, ^{234}Th and ^{234m}Pa are removed so a fresh sample would have less background than an older sample of ^{234}Th. This effect is more important for the two-channel system than for the multichannel systems where the spectrum is observed for each measurement. Systems should be checked each shift with SNM samples for standards. More details concerning potential errors can be found in Reference 105.

Data Analysis Requirements

As with other gamma-ray assay methods, a major part of the data analysis is determining the net count rate in the assay peak. The standard technique of subtracting background estimated from a flat region of the spectra is the usual mode of analysis. With a system employing two SCAs, such as the SAM-II, the enrichment I can be determined from

$$I = aC_1 - bC_2 \tag{5-53}$$

where a and b are constants determined from calibration with two standards differing in enrichment and C_1 (peak) and C_2 (background) are the total counts in the two SCA's. For the SAM-II system, fitted calibration constants can be dialed into the instrument, and the enrichment values will be directly displayed. A formula for the relative statistical uncertainty (from counting statistics only) in I is (Ref. 98)

$$\frac{\Delta I}{I} = \frac{\sqrt{a^2C_1 + b^2C_2}}{aC_1 - bC_2} \tag{5-54}$$

To obtain an estimate of the systematic error of this method, the uncertainty of the calibration curve must be determined (Ref. 106).

Survey of Selected Literature

Low Enriched UO_2 Powder (Ref. 103)

The isotopic abundance of ^{235}U of low-enrichment UO_2 powder (0.2% to 4.4% ^{235}U) in 5-gal. containers was determined. A 2-in. diameter, 0.5-in. thick NaI detector was used with a two-channel system, which displayed the enrichment on a front panel meter through the application of Eq. 5–53. The collimated detector viewed the bottom of the containers. Two containers of 0.71% and 2.38% enriched U were used as standards for the measurements on 17 other containers.

The results for 14 containers were within the uncertainty of the stated enrichments of 1% to 3% (2σ). The statisical uncertainty of the enrichment measurements was less than 1.2% (2σ).

Low-Enriched UF_6 (Ref. 101)

UF_6 in 2.5-ton cylinders (type 30A and 30B) with enrichments ranging from 1.3% to 3.1% for 107 cylinders was measured. An Eberline SAM-II portable NaI (5-cm diameter, 1.3-cm thick) unit was used. Two 10-cm diameter cans of U_3O_8 powder of 0.71% and 10% enrichments were used as standards for an initial calibration of the system prior to the field measurements. The calibration was checked against additional U_3O_8 standards. The check indicated a ±3% (relative) accuracy. Iron plates, 1 cm thick, were used to simulate the cylinder walls. The wall thicknesses were measured to ±0.05 mm with an ultrasonic gauge.

The precalibrated system was then used to measure the cylinders. Paint on the measured portion of the cylinder walls was removed before the detector was used. The cylinders were counted for 5 min each, and six cylinders could be measured per hour.

Statistical uncertainties for a 5-min count of U_3O_8 standards measured through the 1-cm plate ranged from 4% for 0.71% ^{235}U to 0.5% for 10.0% ^{235}U. The initial results of the field measurements on the UF_6 cylinders showed a +3% bias relative to mass spectrometric values. The calibration constant was adjusted to account for this bias in further measurements. The measured enrichments of 89 of the 107 cylinders agreed within 16% of the stated ("tag") value. Within this range, the standard deviation of $[(I_{NDA} - I_{TAG})/I_{TAG}] \times 100$ was 5.3% with a mean value of 0.3% for the ratio.

The most likely cause of the large differences observed for the remainder of the cylinders was plate-out of ^{234}Th from previous UF_6 fillings leading to significant changes in background radiation resulting from the ^{234m}Pa daughter of ^{238}U.

Enriched UF_6 (Refs. 101 and 102)

The material assayed was UF_6 with enrichments ranging from 3.1% to 97.7% in 5-in. diameter, steel and monel 8-L cylinders (type 5A); 24 cylinders were measured.

The procedure was identical to that in the preceding application except that counting time per cylinder was 1 min, and a monel cylinder containing U enriched to 58.3% ^{235}U was used as a standard. Twenty cylinders would be measured in 1 h.

Because of the thinner wall (0.6 cm) of the cylinder and the higher 186-keV gamma-ray activity relative to background, more precise results were obtained than in the assay of type 30 cylinders. For all cylinders, the standard deviation of the measured enrichments from the "tag" values $[(I_{NDA} - I_{TAG})/I_{TAG}] \times 100$ was 3.2% decreasing to 2.1% for 19 steel and monel cylinders with enrichments greater then 7%. The average NDA value differed by +0.9% from the "tag" value.

A similar result, 3.4% (1σ), was reported for 50 UF_6 cylinders with >20% ^{235}U. The average NDA value differed by −0.8% from the tag value. These later measurements were taken to verify U inventories at a facility.

Incinerator Ash (Ref. 104)

The material assayed was incinerator ash, 80% U by weight, in 15.9-cm diameter by 38.8-cm long cans. The "tag" enrichments of the 16 cans measured varied from 1.2% to 4.8%.

The cans were positioned 31 cm above a Ge(Li) detector so that the detector viewed the entire top or bottom of the can. Two 10-cm cans of U_3O_8 powder of 0.75% and 10.06% enrichment were used as standards to calibrate the system. A correction was made for the different areas of the standard and sample cans.

Counting times of 5 min resulted in counting errors of less than or equal to 1%. Large differences from "tag" values were observed in enrichments measured at the top and bottom of the residue cans. Measurements of several cans indicated enrichments of 16% to 18% at the bottom and 2.6% to 2.8% at the top. One can was sampled at both top and bottom positions, and the mass spectrometric analyses were in agreement with the enrichment meter measurements.

MOX Pellets (Ref. 99)

Four Pu recycle fuel pellets with mass fractions Pu/(Pu + U) ranging from 0.0163 to 0.0916 were measured. A Ge(Li) detector system was used for 50-min counts of the 208-keV gamma ray from the ^{237}U daughter of ^{241}Pu. One pellet was used for a standard. The ratio of ^{241}Pu to total Pu was known for all pellets.

The measured Pu/(Pu + U) mass fraction differed by −0.4% to −0.7% (average = −0.6%) from the reported mass fractions. The uncertainty of each determination was 0.3% to 0.4%.

MOX Powder (Ref. 100)

The material assayed was mixed natural U and Pu oxide powders. The mixtures were made by gravimetrically combining separate batches of UO_2 and PuO_2 powders or by using coprecipitated mixed oxides to obtain different Pu mass fractions ranging from 2.0 to 17.2 weight percent. Different Pu isotopic compositions were used with ^{239}Pu percentages varying from 70.91 to 87.12 weight percent. The material was contained in 0.5- or 1.0-L polyethylene bottles, which were bagged and enclosed in a metal can. Total sample mass was about 2 kg.

A collimated Ge(Li) detector was used with a multichannel analyzer system. The detector was a 70 cm^3, 13% efficient detector with 1.5-keV FWHM resolution at 1.0-MeV and 770-eV resolution at 122 keV. The samples were assayed inside a shielded cave and were rotated and translated vertically.

To test the enrichment meter principle, the net count rate of seven different (U,PuO_2) mixtures was measured for the 148.6-keV ^{241}Pu and 413.69-keV ^{239}Pu gamma rays and plotted as a function of the product of isotope abundance and Pu mass fraction. The data were fit well by a straight line with zero intercept.

For the MOX sample with 12% Pu weight fraction, the Pu isotopic abundances could be determined as in Table 5.30.

Table 5.30 Isotopic abundances in MOX sample with 12% Pu weight fraction

Isotope	Abundance (%)	Gamma-ray Energy (keV)	Precision (1σ) (%)
^{238}Pu	0.44	152.7	1.0
^{239}Pu	70.41	413.7	0.3
^{240}Pu	21.54	642.6	4.3
^{241}Pu	5.20	148.6	0.3

Uranium Metal (Ref. 105)

A SAM-II unit NaI crystal (5-cm diameter by 1.3-cm thick) was used to verify the enrichment of U metal (93% ^{235}U). All assayed items were compared to one item chosen as a standard. For 29 items, the ratio [(NDA − TAG)/TAG] × 100% varied by 1.89% (1σ) with a mean value of 0.66%. These measurements were taken to verify U inventories at a facility.

5.3.1.2 Gamma-ray Ratios

Description of Method

The method of gamma-ray ratios uses the fact that most isotopes in SNM emit gamma rays with measurable intensities. Ratios of the areas of gamma-ray peaks in Ge multichannel spectra can be used to determine the isotopic ratios. If ratios are measured that involve all the isotopes present, then the total isotopic composition of the material can be determined nondestructively. For example, suppose that an item containing two isotopes is counted with measured gamma-ray intensities I_1 and I_2 from isotopes 1 and 2. Then

$$\frac{I_1}{I_2} = \frac{\varepsilon_1}{\varepsilon_2} \cdot \frac{(t_{1/2})_2}{(t_{1/2})_1} \cdot \frac{\text{Br}_1}{\text{Br}_2} \cdot \frac{N_1}{N_2} \qquad (5-55)$$

where

ε_1 and ε_2 = peak efficiencies for gamma rays 1 and 2 (including detector and geometric efficiency and absorption effects)
$(t_{1/2})_1$ and $(t_{1/2})_2$ = half-lives for isotopes 1 and 2
Br_1 and Br_2 = branching fractions for gamma rays 1 and 2
N_1 and N_2 = numbers of atoms of isotopes 1 and 2

The branching fractions and half-lives are known constants, so Eq. 5−55 reduces to

$$\frac{I_1}{I_2} = \frac{\varepsilon_1}{\varepsilon_2} \cdot \frac{N_1}{N_2} \cdot K \qquad (5-56)$$

where

$$K = \frac{(t_{1/2})_2}{(t_{1/2})_1} \cdot \frac{\text{Br}_1}{\text{Br}_2}$$

The relative efficiency $\varepsilon_1/\varepsilon_2$ is the only parameter than is needed to convert the measured gamma-ray ratio into an isotopic ratio. If only two isotopes, 1 and 2, are present, then the atom percent of isotope 1, is

$$\frac{N_1}{N_1 + N_2} = \frac{1}{1 + (\epsilon_1 I_2/\epsilon_2 I_1) K} \qquad (5\text{–}57)$$

and similarly for isotope 2.

If the gamma-ray energies are close enough, ϵ_1/ϵ_2 will equal 1.0, but usually the energies are far enough apart that this ratio should be determined. This is done by measuring for each item the intensities of different gamma rays from a single isotope. Dividing each peak area by the known branching fraction defines the relative efficiency at different energies. A smooth curve is fitted to these data, and the ratio ϵ_1/ϵ_2 is calculated. Wider ranges of relative efficiencies can be determined by matching relative efficiency curves from different isotopes at a given energy. In Figure 5.31, an example is plotted of a relative efficiency curve determined by ^{239}Pu, ^{241}Pu, and ^{241}Am gamma rays.

The gamma-ray ratio method assumes that the isotopic composition of material throughout the container is uniform, but is independent of chemical inhomogeneities. This method can be used to determine isotopic compositions without the need for calibration standards. The relative efficiency curve of the sample itself provides sufficient information if measurable gamma-ray intensities are present. Further discussion of the limitations in the gamma-ray ratio method may be found in Parker and Reilly (Ref. 107). Gamma-ray ratio techniques as applied to Pu and U are outlined in the following paragraphs.

Plutonium

The isotopic composition of the Pu sample is determined by measuring isotopic ratios involving ^{238}Pu, ^{239}Pu, ^{240}Pu, and ^{241}Pu and assuming the relationship

$$R_{238} + R_{239} + R_{240} + R_{241} + R_{242} = 1 \qquad (5\text{–}58)$$

where R_i is the weight (or number) fraction of each isotope.

A limitation in the method is that ^{242}Pu emits no useful gamma rays. The resultant isotopic abundances determined by gamma radiation will thus be biased unless the amount of ^{242}Pu can be estimated. However, for low-burnup Pu the ^{242}Pu fraction is small. Correlations between ^{242}Pu and ^{239}Pu and ^{241}Pu abundances may be used as predictors of the ^{242}Pu content for $R_{242} \leqslant 5\%$. In that case, the error in the estimate of the ^{242}Pu abundance will have a relatively small effect on other abundance determinations (Refs. 96, 107, and 108).

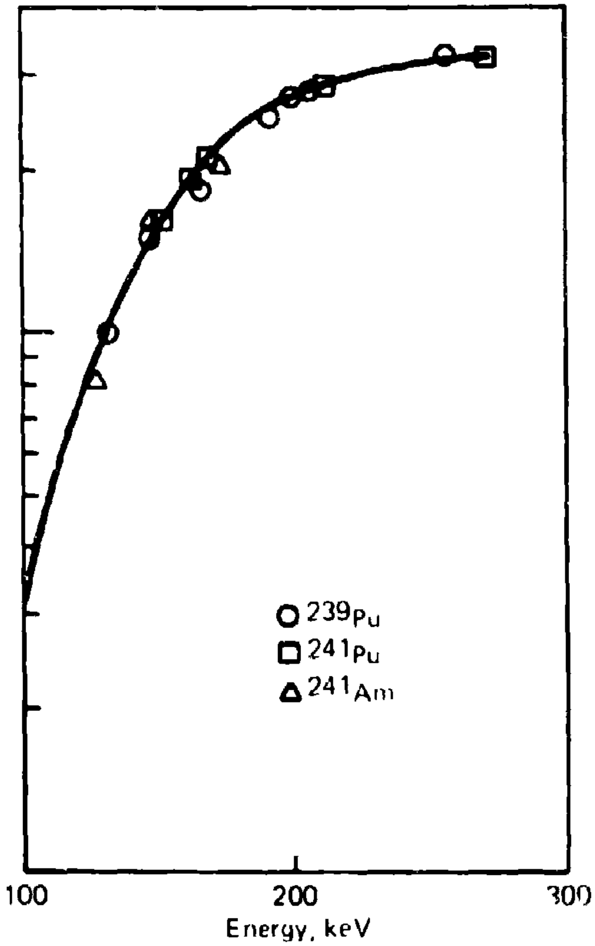

Figure 5.31 Relative efficiency curve obtained from measurements made on a 910-g MOX sample with a small intrinsic Ge detector. The curve is typical of those obtained from the low energy region using this type of detector. (Ref. 93)

The isotopic information supplied by the gamma-ray ratio method allows for a determination of Pu content of containers in conjunction with calorimetric measurements, if the amount of all significant power-generating species is known. Thus, the ^{241}Am content relative to Pu must also be known and an ^{241}Am/Pu isotopic ratio measurement will be necessary for that application.

The complexity of the gamma-ray spectra of Pu samples permits a number of possible gamma-ray pairs to be used for isotopic determinations. A typical Pu gamma-ray spectra is shown in Figure 5.32. Certain special features of Pu spectra allow for a categorization into three energy regions: >125 keV, 94 to 104 keV, and <60 keV. Gamma-ray ratios measured by Ge detectors in the energy region greater than 125 keV have been routinely used for isotopic determinations. Some of the Pu peaks in this region are well separated, requiring only summation over a well-isolated peak followed by subtraction of a smooth background. Others require subtraction of contributions for other isotopes that happen to have nearly the same gamma-ray energy and are unresolvable by even the Ge detectors of highest resolution. Listed in Table 5.31 are gamma rays that have been used for Pu isotopic ratio determinations in this region. The gamma rays listed in this table are either gamma rays used directly in ratio determinations, interfering gamma rays the contribution of which to a peak area must be subtracted away, or gamma rays used for relative efficiency determinations (^{239}Pu and ^{241}Pu) from 129 to 414 keV. A more extensive compilation of Pu and Am gamma rays useful for isotopic ratios can be found in a report by Gunnink, Evans, and Prindle (Ref. 110). The 125, 160, 208, 332, and 335 keV groups of gamma rays each have several unresolved contributors to a peak area. The portion attributable to a specific isotope can be determined, however. Specific gamma-ray pairs that have been used for isotopic determination are listed in Table 5.32. A limitation on measurements in this region is the long counting times (hours) required to obtain data on a sufficient number of gamma ratios.

Another region of gamma-ray spectra that can be used for Pu ratio determinations is in the 94- to 104-keV range. The gamma intensities and energies in this region and at lower energies are listed in Table 5.33. As can be seen in Figure 5.33, the gamma-ray spectrum in this region is very complex with contributions from ^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu, ^{241}Am, and X-rays. A method of unfolding the spectra in this region has been developed by Gunnink (Ref. 115). Ratios of fitted response spectra from each isotope rather than individual peak areas are determined. This technique has been applied to the measurement of low burnup Pu in solids and in solutions. The use of specific gamma-ray peaks in this region for ratio determinations is discussed by Dragnev and Damjanov (Ref. 112). The impetus to measure ratios in this complex region arises from the fact that the branching intensities in all isotopes of interest are higher than the most intense gamma-rays in the >125-keV region. In the case of ^{238}Pu and ^{240}Pu, the intensities are 8 and 17 times higher, respectively. Thus, shorter counting times can be used to obtain sufficient statistics. An estimate of Pu content of solutions using this region is discussed in Section 5.3.1.3.

Also listed in Table 5.33 are the energies and branching intensities of gamma rays with energy less than 60 keV. The intensity of ^{241}Am deter-

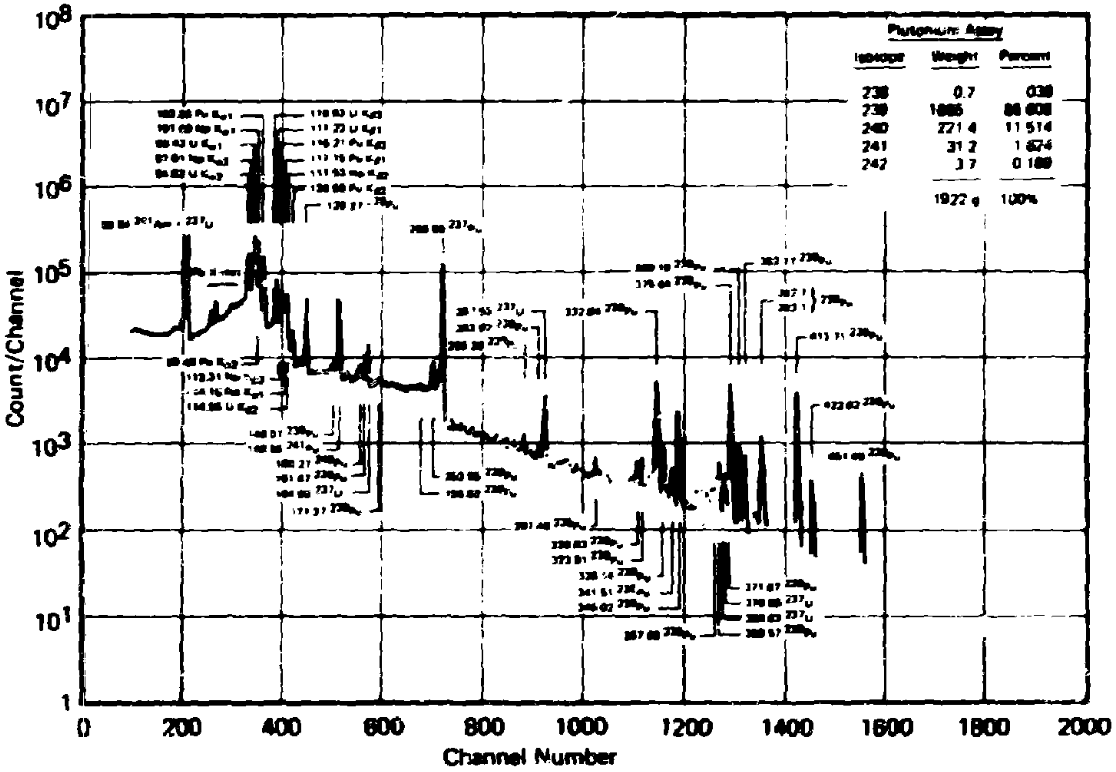

Figure 5.32 Plutonium nitrate gamma-ray spectrum taken with a Ge(Li) detector (from Cline (Ref. 109)).

Table 5.31 Plutonium and Am gamma rays for isotopic and relative efficiency determinations[a] ($E_\gamma \geq 125$ keV)

Isotopes	E (keV)	Gamma Ray Branching Franction (Br) ($\times 10^8$ γ/dis)	Error in Br (%)
^{238}Pu	152.68	956	0.5
^{239}Pu	124.51	61.3	3
	125.21	71.1	2
	129.29	6262	0.2
	144.21	283	0.6
	160.19	6.20	20
	161.45	120	0.4
	171.34	110.5	0.8
	179.19	65.8	1
	189.32	83.0	2
	195.66	106.4	0.5
	203.54	560	0.2
	255.38	80.5	2
	297.49	50.2	2
	332.84	506.0	0.2
	336.11	113.4	0.3
	345.01	559.2	0.2
	375.04	1570	0.1
	413.71	1489	0.1
	645.97	14.89	0.4
	658.93	9.69	0.7
^{240}Pu	160.28	402	0.7
	642.48	12.45	1
^{241}Pu	148.57	187	0.3
	159.96	6.74	—
	164.58	45.3	0.6[b]
	208.00	533	0.3[b]
	267.50	18.2	0.6[b]
	332.35	29.8	0.6[b]
	335.40	2.39	1.1[b]
^{241}Am	125.29	4080	0.5
	164.58	66.7	3
	208.00	791	0.5
	332.35	149.0	0.3
	335.40	496.0	0.3
	662.42	364	0.3
	721.99	196	0.4

[a] Values from Gunnink, Evans, and Prindle (Ref. 110).

[b] From ^{237}U in equilibrium with ^{241}Pu. About 1 month required after Pu separation to reach within 5% of equilibrium.

Table 5.32 Some Pu and Am gamma-ray pairs used to determine isotope ratios

Isotope	Isotopic ratio	Gamma Rays (keV)	Comments	Ref.
^{238}Pu	^{238}Pu/^{241}Pu	152.7/148.6	Longer counting times required for 152.7 keV for very low burnups	107, 111, 112
	^{238}Pu/^{239}Pu	152.7/144.2		113
^{240}Pu	^{240}Pu/^{241}Pu/(^{237}U)	160.3/164.6	^{241}Pu 160-keV line swamps ^{240}Pu at higher burnups	6, 107, 111 112
	^{240}Pu/^{239}Pu	642.5/646.0	Sometimes used in lieu of 160/164 if a larger detector is available	93, 113, 114
^{241}Pu	^{241}Pu/^{239}Pu	148.6/144.2	144.2 difficult to measure for reactor grade Pu	113
	^{241}Pu/^{239}Pu	148.6/129.3	No ^{237}U equilibrium required for 148.6 keV	107
	^{241}Pu(^{237}U)/^{239}Pu	208.0/203.5	^{237}U equilibrium required for 208 keV	107, 113
	^{241}Pu(^{237}U)/^{239}Pu	332.4/345.0	^{237}U equilibrium required for 332 keV	111
^{241}Am	^{241}Am/^{239}Pu	125.2/129.3	Poor results at low Am concentrations	107
	^{241}Am/^{239}Pu	335.4/345.0		111
	^{241}Am/^{239}Pu	662.4/659.0		113
	^{241}Am/^{239}Pu	662.4/646.0	Suitable for low Am concentrations if larger detector available	111

Table 5.33 Prominent low-energy gamma rays associated with isotopes of Pu and ^{241}Am and the corresponding emission probabilities (γ/dis)[a]

Energy	Isotopes					
	^{238}Pu	^{239}Pu	^{240}Pu	^{241}Pu	^{237}U[b]	^{241}Am
43.477	3.92×10^{-4}	—	—	—	—	—
45.232	—	—	4.53×10^{-4}	—	—	—
51.629	—	2.70×10^{-4}	—	—	—	—
59.536	—	—	—	—	—	0.359
94.660	1.05×10^{-6}	4.22×10^{-5}	6.36×10^{-7}	3.03×10^{-6}	—	—
96.150	—	2.23×10^{-7}	—	—	—	—
97.071	—	—	—	—	3.89×10^{-6}	1.18×10^{-5}
98.441	1.69×10^{-6}	6.76×10^{-5}	1.02×10^{-6}	4.85×10^{-6}	—	—
98.780	—	1.22×10^{-5}	—	—	—	—
98.951	—	—	—	—	—	2.03×10^{-4}
99.530	Pu Kα₂ X-ray from induced fluorescence					
99.864	7.24×10^{-5}	—	—	—	—	—
101.066	—	—	—	—	6.20×10^{-6}	1.90×10^{-5}
102.966	—	—	—	—	—	1.95×10^{-4}
103.020	—	2.17×10^{-6}	—	—	—	—
103.680	—	—	—	1.01×10^{-6}	—	—
103.748	Pu Kα₁ X-ray from induced fluorescence					
104.244	—	—	6.98×10^{-5}	—	—	—
129.294	—	6.26×10^{-5}	—	—	—	—
148.567	—	—	—	1.87×10^{-6}	—	—
152.680	9.56×10^{-6}	—	—	—	—	—
208.000	—	—	—	—	7.91×10^{-6}	—

[a] From Gunnink and Evans (Ref. 28).

[b] The branching intensities shown for ^{237}U include the α-branching probability of ^{241}Pu. The values, therefore, represent photon emission probability per decay of ^{241}Pu, assuming α decay equilibrium has been established.

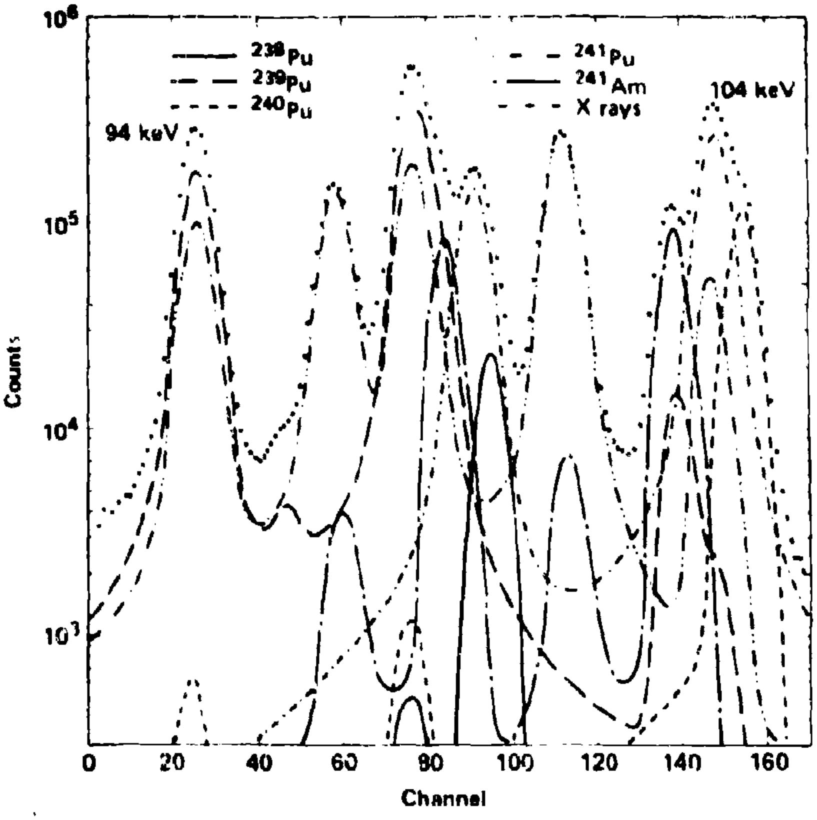

Figure 5.33 The 94- to 104-keV peak multiplet of a low-burnup weapons-grade Pu oxide sample. This is a very complex region, consisting of up to 14 X-rays and gamma rays that must be interpreted for the isotopic analysis of aged Pu samples. For solutions, the Pu X-ray contribution from α-induced fluorescence will be substantially less than is shown here. The dotted line represents actual data. [from Gunnink and Evans (Ref. 28.)]

mines whether these peaks, the most intense gamma-ray branches of ^{238}Pu, ^{239}Pu, and ^{240}Pu, can be used. Isotopic ratios of recently processed Pu can be determined using these gamma rays and higher energy gamma rays. However, the high background resulting from the in-growth of the intense 59.5-keV ^{241}Am line eventually obliterates the peaks with less than 60-keV energy.

Uranium

Application of the gamma-ray ratio technique has been applied to the measurement of ^{235}U/^{238}U isotopic ratios. The ^{238}U part of the ratio is determined by gamma rays emitted by ^{234}Th or ^{234m}Pa daughters. If the daughter gamma rays are in equilibrium with the ^{238}U parent activity, then these daughter radiations provide a measure of the ^{238}U content. About 160 days are required for the daughter activity to be within 1% of ^{238}U. Table 5.34 lists some gamma rays from ^{234}Th, ^{234m}Pa, and ^{235}U that can be used for this determination. As can be seen from this table, there are no gamma-ray peaks of ^{235}U lying close to those of ^{234m}Pa and ^{234}Th. However, Harry, Aaldijk, and Braak (Ref. 116) were able to use most of the ^{235}U gamma rays listed for an estimate of the ^{235}U enrichment.

The measured gamma-ray intensities are used with the Table 5.34 data to determine a joint efficiency curve for ^{235}U and ^{238}U gamma rays by least-squares fitting. As part of the fitting procedure, a multiplicative constant k times the ^{235}U curve is used to adjust the ^{235}U curve so that it smoothly matches the ^{238}U curve. The U enrichment $\bar{I}$ is then given by

Table 5.34 Values of the gamma-ray abundances of ^{235}U, ^{234m}Pa, and ^{234}Th[a]

Isotope	Energy (keV)	Br (γ/dis) (% error in Br)[b]
^{235}U		
	143.78	0.1067 (0.4)
	163.36	0.0506 (0.5)
	185.72	0.576 (0.4)
	194.94	0.00624 (1.0)
	202.13	0.0103 (2.1)
	205.31	0.0494 (0.5)
^{234m}Pa		
	258.30	0.000770 (0.8)
	742.30	0.000870 (2.0)
	766.50	0.00343 (1.2)
	1001.40	0.00889 (0.7)
	1738.5	0.000242 (3.0)
	1831.9	0.000179 (4.8)
^{234}Th		
	63.33	0.0425 (4.9)
	92.367[c]	—
	92.792[c]	—

[a] Taken from Ref 116.

[b] The error is the external relative standard deviation (in %).

[c] Dragnev and Damjanov (Ref. 112).

Source: Ref. 116

$$I = \left[1 + k \frac{t_{1/2}(238)}{t_{1/2}(235)}\right]^{-1} \qquad (5\text{-}59)$$

A close-lying group of radiations suitable for use for ratio measurements of $^{235}U/^{238}U$ has been identified by Dragnev and Damjanov (Ref. 112). The intensity of the 93.35-keV Th $K\alpha_1$ X-ray is used as a measure of the ^{235}U content, and the sum of the intensities of the 92.367 and 92.792 ^{234}Th gamma rays is used for ^{238}U. A Ge detector is used to measure these peaks from calibration standards, the 93.35/(92.367 + 92.792) ratio is calculated, and a calibration curve suitable for assays of unknowns is determined.

Scope of Applications

The primary use of the ratio method is the measurement of Pu and U isotopic abundances and the Pu content of sealed containers.

Plutonium

The gamma-ray ratio method can be used for any type of Pu-bearing material that is isotopically homogeneous and that has sufficient gamma-ray intensity. The isotopic compositions of nitrate solutions, oxides, and various forms of heterogeneous scrap with Pu contents ranging from less than 0.1 g to kilograms are routinely measured. The Pu content of solid samples can be determined using the gamma-ray ratio method in conjunction with calorimetry. The Pu content of the wide variety of scrap categories and feed materials is routinely verified with the gamma-ray ratio and calorimetry techniques.

Uranium

The use of the gamma-ray ratio method for measurement of the ^{235}U enrichment of U-bearing materials has been investigated. Materials such as pellets, powder, scrap, and solutions have been measured. The best results were obtained for enrichments less than 8%. Because of the low activity of ^{238}U, larger quantities of U are needed to make a $^{235}U/^{238}U$ determination than are needed for a Pu determination.

Summary of Performance

See Table 5.35 for a summary of performance.

Equipment

The detector resolution is very important for this method for Pu because many gamma rays that are only several keV apart need to be

Table 5.35 Summary of performance: gamma-ray ratios[a]

Sample Type	Isotopic Composition (%)	Gamma Rays Used (keV)	Counting Time	Performance (% RSD)		Comments	Ref.
				Random Error	Systematic Error		
Plutonium:							
PuO_2 powder	0.01 ^{238}Pu	94 to 104 complex	4 min	^{238}Pu: 5.1	—		117
	93.7 ^{239}Pu			^{239}Pu: 0.17	—		
	5.8 ^{240}Pu			^{240}Pu: 2.3	—		
	0.44 ^{241}Pu			^{241}Pu: 1.2	—		
	0.1 ^{241}Am			^{241}Am: 2.5	—		
		94 to 104 complex	600 min	^{238}Pu: 0.7	—		117
				^{239}Pu: 0.013	—		
				^{240}Pu: 0.2	—		
				^{241}Pu: 0.1	—		
				^{241}Am: 0.4	—		
	Isotopic composition similar to above	94 to 104 complex	Several hundred minutes	^{238}Pu: —	2.5[b]		117
				^{239}Pu: —	0.03		
				^{240}Pu: —	0.62		
				^{241}Pu: —	1.3		
				^{241}Am: —	4.0		
Pu reference materials and other	70 to 94 ^{239}Pu	9 ratios in 125 to 662-keV range	50,000 s	$^{238}Pu/^{241}Pu$: 1.6 to 7.6	2.4	2-detector system	93
				$^{240}Pu/^{239}Pu$: 2.1 to 3.7	2.0		
				$^{241}Pu/^{239}Pu$: 1.2 to 2.7	1.3		
				$^{241}Am/^{239}Pu$: 1.3 to 2.0	1.2		

Note—See footnote at end of table.

Table 5.35 Summary of performance: gamma-ray ratios[a] (Cont'd)

Sample Type	Isotopic Composition (%)	Gamma Rays Used (keV)	Counting Time	Performance (% RSD)		Comments	Ref.
				Random Error	Systematic Error		
Mixed oxide, rods, pellets, Pu standard reference materials		332/336/345	1000 s	^{239}Pu/^{241}Pu: 1.3 to 1.6	—	Large Ge(Li) (16%)	111
PuO$_2$ powder, 12 kg		332/336/345	1000 s	^{239}Pu/^{241}Pu: 3.7 ^{241}Am/^{239}Pu: 9.0	— —	Small hpGe, field test	111
		148/153,160/164, 332/336/345	360 min	^{238}Pu/^{241}Pu: 3.6 ^{239}Pu/^{241}Pu: 1.1 ^{240}Pu/^{241}Pu: 3.9 ^{241}Am/^{239}Pu: 2.4	— — — —	Small hpGe, field test	111
Uranium:							
Oxide powder, pellets, scrap, 307 to 2263 g U	0.2 to 20 ^{235}U	^{235}U, ^{234m}Pa Gamma rays in 143 to 1832-keV range	—	^{235}U/U: —	6[b]		116
UO$_2$ pellets, Al clad	0.4 to 3.9 ^{235}U		—	^{235}U/U: —	7[b]		116
Powder, pellets	1.8 to 4.0 ^{235}U	92.4 to 93.4-keV range	—	^{235}U/U: —	<1		112

[a] All data from literature survey.

[b] Errors listed are the standard deviation between ratio and mass spectrometric results.

resolved. Usually only one detector size is chosen for the measurement, depending upon which region of the spectrum is of interest, but simultaneous measurement of a sample with two detectors of different sizes has been done (Ref. 93). High-resolution Ge detectors are also required for U isotopic determinations. Manufacturers are continually improving resolution and increasing the size of their Ge detectors. The resolution requirements quoted in this section can be met with currently available detectors.

The electronics required for this method consists of a stable high-voltage supply, preamplifier, amplifier, pulse pileup rejector, an A/D converter, and a multichannel analyzer (4096 channels). A small computer can be used for peakfitting and analysis, which would be impractical to do by hand. When peakfitting is not used (for the higher energy region), a multichannel analyzer will suffice. The capability for reading out the data from a multichannel analyzer onto paper, magnetic tape, or disk allows the transfer of the data to a computer for analysis.

The 1-cm^3 high-purity Ge detectors suitable for these measurements cost $7000 to $10,000. The larger Ge(Li) detectors cost $10,000 to $15,000. A complete system, including a small computer, will cost about $50,000.

Mechanically the systems are very simple. A sample is placed near the detector and counted. The detector should be shielded with Pb to decrease room background. A Pb filter (1 to 3 mm) can be placed between the detector and sample to reduce lower energy gamma rays if only the region above 300 keV is of interest. If the region 100- to 200-keV is of interest, 0.5 to 1.0 mm of Cd can be used to reduce the intensity of lower energy gamma rays, especially the 59.5-keV gamma ray from ^{241}Am. For the analyses that use part of the gamma-ray spectrum below 100 keV, plastic containers are preferred because metal containers can attenuate these gamma rays strongly. The effects of the container wall and absorbers are part of the relative efficiency function for either type of container.

Major Sources of Error

For both Pu and U, an important consideration is obtaining sufficient counting statistics to obtain sufficient precision in the estimates of gamma-ray ratios. The maximum count rate must be kept below a certain rate, typically several thousand counts per second, or otherwise the resolution of the Ge detectors will deteriorate. Other possible sources of error and interferences for each element are described in this section.

Plutonium

For some isotopic compositions of Pu it is difficult to obtain a precise estimate of an isotope because of its relatively weak gamma-ray intensity. In the 94- to 104-keV region, the ^{239}Pu intensity from low-burnup Pu is high enough relative to neighboring peaks to obtain good results in short counting times. However, for higher burnup reactor grade material, the ^{239}Pu intensity has decreased enough so that other energy regions must be used (Ref. 117). Conversely, the ^{238}Pu content in low burnup material is so low that long counting times (hours) are required to obtain sufficient statistics, and in higher burnup material, the increased ^{238}Pu content will allow shorter counting times.

For overlapping peaks where only one component is of interest, any relative increase in other isotopic contributions from other isotopes resulting from differing Pu isotopics leads to loss of precision. For example, the 160-keV peak is a composite of gamma rays from ^{239}Pu, ^{240}Pu, and ^{241}Pu. For increasing burnups, the ^{241}Pu contribution grows in faster than does that from ^{240}Pu, and the resultant error from subtracting this large contribution leads to a poorly characterized ^{240}Pu abundance (Ref. 112).

The spectral peaks used for ^{241}Pu determination are, in some cases, actually radiations from its ^{237}U daughter ($t_{1/2}$ = 6.75 days). About 29 days are required before equilibrium to within 5% is reached. A correction may be made if the previous Pu-U separation time is known.

The ^{241}Am activity affects all the gamma-ray measurements in blotting out low-energy radiations (<60 keV), increasing the count rate so that longer times are needed to count higher energy (> 60 keV) gamma rays, and complicating the spectral analysis of the higher energy gamma rays due to the larger number of higher energy Am gamma rays and sum peaks. The intensity of the extraneous 60-keV radiation may be reduced by using a suitable absorber. Plutonium recovered from irradiated fuel elements can contain 10 μCi of fission products per gram of Pu. At this concentration, fission product gamma rays from ^{95}Zr–^{95}Nb will swamp the 600-keV peaks and reduce the signal-to-background ratios for the lower energy gamma rays.

Uranium

Since the ^{238}U portion of the measured ^{235}U/^{238}U ratio results from measurements of ^{234m}Pa daughter radiation, the daughter activity must be in equilibrium with the ^{238}U activity, or the time since the last decay-chain-breaking U separation must be known. For a sample with an unknown history this time may be determined by measurements taken at least 13 days apart (Ref. 118). The ^{235}U/^{238}U ratio cannot be determined for MOX samples because the Pu gamma rays dominate the spectrum.

Measurement Control Requirements

Under optimum conditions, the technique is self-calibrating because gamma rays from each sample can be used to generate a calibration curve for that sample. The form of the calibration curve has already been discussed in this section. As a check of the method, standards consisting of samples of standard reference materials (NBS 946, NBS 947, and NBS 948) can be used. This could be done as a check of the initial operation of the system but would not be required routinely. In lieu of the SRMs, well-characterized samples (isotopic distribution known from mass spectrometry and alpha counting) can be used. The measured isotopic abundances of these materials should agree with the declared values.

Data Analysis Requirements

The major part of the data analysis effort in the gamma-ray ratio method is the determination of Ge peak areas. The sophistication required for this step of the data analysis is dependent on the complexity of the spectra used to determine the isotopic ratios as well as the accuracy required. For all isotopes of interest for Pu and Am, sets of gamma-ray ratios exist that require only summation over the peak areas and determination of a simple background correction (Ref. 112). If only one well-separated peak pair is of interest, then a programmable calculator might suffice, but for a large number of repetitive measurements or for analysis of overlapping gamma rays and for maximum reliability, a multichannel analyzer interfaced with a minicomputer with mass storage capability is a necessity.

The more complicated cases of overlapping gamma-ray peaks require unfolding of the spectrum into contributions from each isotope. This can be accomplished by resolving the spectrum into a group of overlapping gaussian peaks with different energies and areas. The greatest level of sophistication is required in the 94- to 104-keV and 630- to 670-keV regions where multiplets composed of 14 peaks occur in both. The complex spectrum shown in Figure 5.33 was unfolded by fitting the known spectral groups of Pu and ^{241}Am rather than individual peaks to obtain the relative isotopic contributions.

Once the relative efficiency curve has been determined by least-squares fitting of the appropriate empirical function to the relative gamma-ray intensities, and the peak areas of the isotopes of interest have been calculated, then the isotopic ratios or abundances can be computed using Eq. 5–55.

Data analysis programs specifically developed for Pu isotopic analyses at U.S. national laboratories and facilities will yield accurate and reliable results. One such program (GRPNL2) is run on a 32K 16-bit minicomputer (PDP 11/34) and will output the isotopic composition of an unknown sample in about 12 min.

Survey of Selected Literature

PuO_2 Powder (Ref. 117)

The isotopic composition of PuO_2 powder in 1- to 2-kg lots containing 94% ^{239}Pu and 0.01% to 0.2% ^{241}Am was measured. The 94- to 104-keV region was measured with a 1-cm^3 Ge detector and analyzed for all Pu isotopes and ^{241}Am using the ratio method. A performance summary is given in Table 5.36.

Table 5.36 Summary of performance: gamma-ray assay system

Isotope	Abundance (%)	Precision (% RSD) for different counting times			Mass Spec-Gamma Ray Ratio
		4 min	120 min	600 min	(% RSD)
^{238}Pu	0.01	5.1	2.0	0.7	2.5
^{239}Pu	93.7	0.17	0.03	0.013	0.03
^{240}Pu	5.8	2.3	0.5	0.2	0.62
^{241}Pu	0.44	1.2	0.2	0.1	1.3
^{241}Am	0.1	2.5	0.4	0.4	4.0

Various Plutonium-Bearing Materials (Ref. 93)

Varieties of Pu reference materials and samples were measured with Pu contents ranging from tenths to hundreds of grams. Samples were counted simultaneously with two detectors: one small (1 cm^3) intrinsic Ge for the 120- to 300-keV region and a 14% Ge(Li) for the 300- to 700-keV region. Count rate was limited to less than 10,000 counts/s. The data were analyzed on a PDP 11/34 using the GRPNL2 program.

The results shown in Table 5.37 were observed over a wide range of Pu contents and isotopic compositions. It was concluded that ^{238}Pu, ^{239}Pu, and ^{241}Pu could be determined with the greatest precision in the <300-keV energy region, and ^{240}Pu and ^{241}Am could best be determined in the 640-keV region.

PuO_2 Powder (Ref. 111)

Ten cans of PuO_2, each containing 1 to 2 kg PuO_2, were assayed. A portable system consisting of a 1-cm^3 Ge detector and microprocessor-based data acquisition system was used (1) with 1000-s counting times to verify the $^{239}Pu/^{241}Pu$ and $^{241}Am/^{239}Pu$ ratios using the 332- to 345-keV complex and (2) with 6-h counting times to verify four isotopic ratios for one can. These measurements were made in support of a safeguards physical inventory at a MOX fuel fabrication plant.

An average precision of 3.7% was observed for the $^{239}Pu/^{241}Pu$ ratio; the declared values agreed within the 2σ counting statistics for all

Table 5.37 Performance of 2-detector gamma-ray assay system

Ratio	Gamma Rays	Precision Ranges (% RSD) 2000 s	Precision Ranges (% RSD) 50,000 s	Systematic Error (% RSD)	Bias $\frac{\text{gamma-ray} - \text{chemical}}{\text{chemical}}$
$\frac{^{238}Pu}{^{241}Pu}$	$\frac{153}{148}$	1.5 to 23 Average: 7.6	0.5 to 7.1 Average: 1.6	2.4	−0.025 ± 0.002[a]
$\frac{^{240}Pu}{^{241}Pu(^{237}U)}$	$\frac{160}{164}$	1.8 to 10.7 Average: 4.9	1.3 to 3.0 Average: 2.1	—	−0.029 ± 0.005
$\frac{^{240}Pu}{^{239}Pu}$	$\frac{642}{646}$	1.2 to 5.7 Average: 3.7	1.4 to 3.2 Average: 2.1	2.0	+0.018 ± 0.005
$\frac{^{241}Pu(^{237}U)}{^{239}Pu}$	$\frac{208}{203}$	1.1 to 4.1 Average: 2.7	0.7 to 2.1 Average: 1.2	1.3	−0.009 ± 0.002
$\frac{^{241}Pu}{^{239}Pu}$	$\frac{148}{144}$	3.6 to 6.4 Average: 4.8	1.0 to 3.8 Average: 2.3	—	−0.002 ± 0.004
$\frac{^{241}Am}{^{239}Pu}$	$\frac{662}{646}$	0.6 to 3.2 Average: 2.0	1.0 to 2.0 Average: 1.3	1.2	−0.001 ± 0.003

[a] Standard error of the mean.

cans. An average precision of 9.0% was observed for the ^{241}Am/^{239}Pu ratio. In addition to the 332 to 345 complex used for ^{239}Pu, ^{241}Pu, and ^{241}Am, the ^{238}Pu/^{241}Pu (153/148) and ^{240}Pu/^{241}Pu (160/164) ratios were measured with the results for a single can as shown in Table 5.38.

Table 5.38 Performance of a portable gamma-ray assay system

Ratio	Precision (% RSD)	$\frac{\text{Gamma-Ray}-\text{Declared}}{\text{Declared}} \times 100$
$\frac{^{238}\text{Pu}}{^{241}\text{Pu}}$	3.6	−3.7 ± 3.4 (1σ)[a]
$\frac{^{240}\text{Pu}}{^{241}\text{Pu}}$	3.9	+0.5 ± 4.0
$\frac{^{239}\text{Pu}}{^{241}\text{Pu}}$	1.1	−2.2 ± 1.1
$\frac{^{241}\text{Am}}{^{239}\text{Pu}}$	2.4	+13.0 ± 2.7

[a] The uncertainty quoted here is from the gamma-ray measurement only.

Various Plutonium-Bearing Materials (Ref. 112)

Plutonium standard reference materials, MOX pellets, and rods were assayed. Nine samples were counted with a 16% Ge(Li) detector for 1000 s. The 332- to 345-keV complex was used to determine the ^{239}Pu/^{241}Pu ratio. Precisions ranging from 1.3% to 1.6% were observed for eight of nine samples counted. The declared isotopic ratio also agreed within the 2σ confidence limits defined by counting statistics for eight of nine samples.

Various Uranium-Bearing Materials (Ref. 116)

Aluminum-clad UO_2 pellets, with nine enrichments of ^{235}U ranging from 0.4% to 3.9%, and U_3O_8 powder, pellets, ammonium diuranate, and scrap in 1-L polyethylene bottles, with enrichments ranging from 0.2% to 20%, were measured. Sample masses ranged from 300 to 2200 g.

The gamma-ray intensities from 63 to 1832 keV for ^{235}U and ^{238}U daughters were measured with a Ge(Li) detector. The enrichment was determined by the gamma-ray ratio technique using Eq. 5–59.

Enrichment measurements of the pellets agreed with declared values to within 7%. A further improvement in precision by a factor of 2 could be obtained by using a collective efficiency curve calculated from several samples. The measured and declared values of the bottled samples agreed within 6% (1σ).

Various Uranium-Bearing Materials (Ref. 112)

Uranium-bearing powder and pellet samples with seven different enrichments ranging from 1.8% to 3.96% ^{235}U were assayed. One gamma-ray multiplet consisting of two gamma rays from ^{234}Th (92.367 and 92.792 keV) and the 93.35-keV Th $K\alpha_1$ X-ray, produced primarily from ^{235}U decay, was used for a gamma-ray ratio determination of enrichment. The spectrum was analyzed using a program suitable for use with a programmable calculator. The ratios were measured for each enrichment, and part of the data was used to determine a calibration curve.

The enrichments predicted by both linear and parabolic fits to the data agreed within 1% of the mass spectrometric values for all samples.

5.3.1.3 Direct Measurement

Description of Method

The determination of isotopic abundances by direct gamma-ray counting uses the measured area under a gamma-ray peak as a measure of the isotopic abundance. The area is transformed into grams of a particular isotope by calibration points or curves, one for each isotope to be determined. From the determination of the isotopic content of a sample and the total elemental content, a measure of the isotopic fraction is obtained. The elemental content is determined from weights of pure compounds, by separate chemical determinations, or by the sum of gamma-ray assays for all isotopes. The samples measured are usually small (tens of milliliters) aliquots of aqueous solutions, measured with reproducible sample-detector configurations. These determinations can be made with Ge or NaI detectors and can provide a rapid, accurate estimate of isotopic abundance. A NaI detector may be used for ^{235}U abundances using the 185.7-keV line, and a Ge detector is generally required if the abundances of ^{238}Pu, ^{239}Pu, ^{240}Pu, and ^{241}Pu are to be determined.

Scope of Applications

Any homogeneous sample type could be measured by this technique as long as its elemental content is known or could be separately measured. The method has been applied to the determination of the ^{235}U enrichment of dissolved samples containing U and the isotopic abundances of different Pu isotopes in reprocessing plant solutions.

Summary of Performance

See table 5.39 for a performance summary.

Table 5.39 Summary of performance: direct measurement of isotopic abundance[a]

Sample Type	Measured System (Gamma Rays) Measured	Sample Concentration (g/L)	Container (Volume)	Total Counting Time	Performance (% RSD)	
					Random Error	Systematic Error
Uranium, low enriched (<5% ^{235}U):						
U oxide	NaI, well (185.7 keV)	80	Sample tube (10 mL)	6000 s	0.3 to 0.6[b]	0.08 to 0.16
U scrap		25 to 100	Sample tube (10 mL)	500 s	4.2[b]	1.1
Plutonium, reprocessed solution:						
0.01% ^{238}Pu, 93% ^{239}Pu, 6% ^{240}Pu, 0.6% ^{241}Pu	hpGe (1 cm^3), minicomputer (43 to 300 keV)	2 to 3	Vial (10 mL)	15 min	^{238}Pu:5 ^{239}Pu:0.05 ^{240}Pu:0.5 ^{241}Pu:2	(c)

[a] All data from users' survey of production facilities.

[b] Reproducibility

[c] Correction made for ^{242}Pu

Equipment

The apparatus required for isotopic determinations by direct counting is similar to that required for other passive gamma-ray methods. Sample preparation may be required, however, that involves chemical transformation of a material into a form that is easily dissolved to prepare a sample suitable for counting. After dissolution SNM concentrations are adjusted to fall within the calibrated range. The small samples are usually placed near or within (for a well counter) the detector in a reproducible counting geometry. This requirement can be met by using a sample holder that is set up in a standard configuration.

As with other gamma-ray systems, the complexity of the spectra to be measured and the amount of information to be extracted dictate the instrumentation/detector that will be required. These range from the NaI (SCA) systems used for the measurement of ^{235}U (185.7 keV) to Ge (multichannel analyzer or computer) systems used for Pu isotopes. A fully computerized Ge system with peripherals is estimated to cost $50,000.

Major Sources of Error

The precautions taken with isotopic measurements of small samples are similar to those used in other gamma-ray systems. Certain aspects, however, require more emphasis. Particular care should be taken to keep aliquot size constant as seen by the detector. The detector/sample configuration should be kept as reproducible as possible because small variations in the sample positioning for high geometry cases can cause large changes in the geometry. Properly prepared small aqueous samples have the advantage of being homogeneous so that matrix inhomogeneity problems are not present, but precautions should be taken to ensure that variations in container wall thickness will not contribute to gamma-ray absorption variability. The presence of any impurity with a high mass absorption coefficient not accounted for by the calibration samples will cause an erroneous low value. Calibration reference materials should be prepared to bracket or match production material absorption properties. Drifts in Ge detector efficiencies (1% changes in several days) have been noted (Refs. 28 and 115). Separate counts of reference samples should be taken to check and correct for this effect, if necessary.

Measurement Control Requirements

Measurement control requirements are similar to those for other gamma-ray systems. More detailed discussions may be found in Sections 5.2.1.2 and 5.3.1.1.

Data Analysis Requirements

The data reduction hardware and software requirements vary with the complexity of the spectra and the number of measurements to be made. A hand calculator may be sufficient for the determination of the ^{235}U isotopic abundance. But if routine measurements are made on many U samples, then computerized data analysis using a minicomputer may be used. For a complete measurement of Pu isotopic abundances, a minicomputer and sophisticated programs are required. More details on this subject may be found in the data analysis parts of Sections 5.2.1.1 and 5.2.1.2.

Survey of Production Facilities

The isotopic abundances of low-enriched U samples and Pu solutions are measured in a few facilities using the direct gamma-ray method. The results from one fuel fabrication facility and a reprocessing plant are described in the following paragraphs.

Uranium

The ^{235}U enrichments of a wide range of low-enriched sample types have been routinely measured in a fuel fabrication facility. Sample types are categorized into pure and impure materials. The sample preparation procedure differs for these two categories. Pure materials, such as oxide powders and pellets, are oxidized to U_3O_8 at 900°C, and weighed amounts of those materials are dissolved to a concentration that matches the calibration reference materials (80 g/L). Impure materials (e.g., scrap) are dissolved and filtered, and their concentrations are adjusted roughly within the calibrated range (25 to 100 g/L). The U concentration is later determined by a chemical method. Aliquots (10 mL) of the samples are loaded into matched polypropylene sample tubes and are counted for 500 s in NaI well counters.

For these accountability measurements two SCAs are used in conjunction with a NaI detector system; one is set to count the 186-keV ^{235}U gamma-ray peak and the other is set to measure 767- and 1001-keV gamma-rays from the ^{238}U daughter. A background correction for the ^{235}U is made using the measured higher energy gamma-ray intensities. Multiple samples of pure production materials serve as reference materials and are measured for twelve 500-s periods; a standard representing impure categories is measured once. The reproducibilities of measurements of reference material solutions with varying enrichments measured over a 3 month period are shown in Table 5.40. Each value reported here is based on at least 25 measurements.

The measurements of the reference materials were used as estimators of the systematic error of the measurement (uncertainties of reference materials were assumed to be negligible). Shown in the third column of Table 5.40 are systematic errors that would be obtained from 16 replicate measurements. Sample insertion into some of the well detectors is handled by automatic loading hardware. Turnaround time for the 12-count sample types is about 3 h.

Table 5.40 Performance of enrichment analyzer system

Reference Material	Reproducibility (% RSD) (ΔT = 3 month)	Systematic Error (% RSD)	Counting Time (s)
1% ^{235}U	0.47	0.12	12 × 500
2% ^{235}U	0.33	0.08	12 × 500
2% ^{235}U	0.62	0.16	12 × 500
3% ^{235}U	0.31	0.08	12 × 500
3% ^{235}U (scrap)	4.24	1.1	1 × 500

Plutonium

The isotopic abundances of ^{238}Pu, ^{239}Pu, ^{240}Pu, and ^{241}Pu from recently reprocessed irradiated fuel are determined by measuring gamma-ray peaks in the 43- to 200-keV region using a 1-cm^3 hpGe detector and associated electronics interfaced with a minicomputer. A 10-mL aliquot of the sample solution containing 20 to 30 mg of Pu in a plastic vial and an outer container is placed on top of the detector and counted for 15 min. A calutron-separated ^{239}Pu reference source is counted before and after a group of sample determinations.

Based on 4 yr of measurements, the following performance was observed:

Isotope	*Precision % (2σ)*
^{238}Pu (0.01%)	10.
^{239}Pu (93. %)	0.1
^{240}Pu (6.0 %)	1.0
^{241}Pu (0.6 %)	4.

The accuracy of the measurements was better than the precision of either this method or mass spectrometry. The hardware and software for this system are described in Ref. 115.

Survey of Exchange Programs

Figures 5.34 and 5.35 are histograms comparing the random error performance of the gamma-ray spectroscopic enrichment measurement technique for ^{235}U with mass spectrometric methods as determined by the

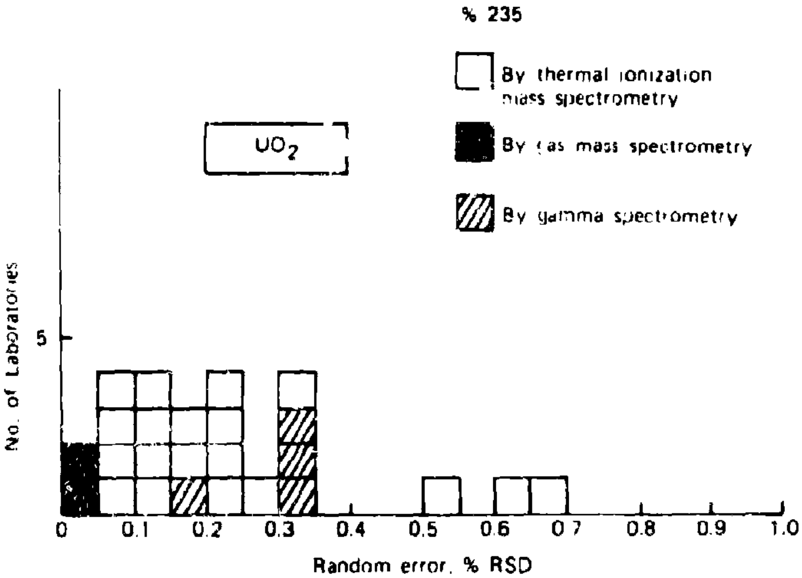

Figure 5.34 Random error of mass spectrometric and gamma-ray spectroscopic methods for low-enriched UO$_2$ powder [from Safeguards Analytical Laboratory Evaluation (SALE) data (Ref. 119).]

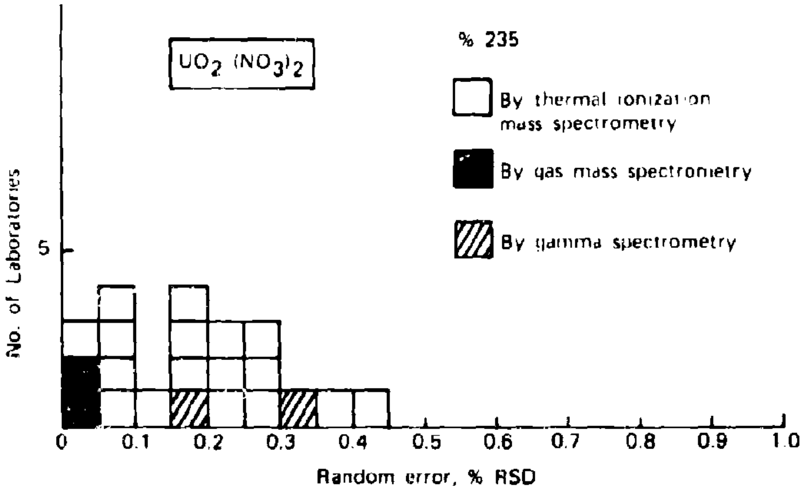

Figure 5.35 Random error of mass spectrometric and gamma-ray spectroscopic methods for uranyl nitrate [from Safeguards Analytical Laboratory Evaluation (SALE) data, Ref. 119).]

Safeguards Analytical Laboratory Evaluation program for uranium dioxide or uranyl nitrate (Ref. 119).

5.3.2 Passive Neutron Enrichment Measurements

Description of Method

Uranium isotopic enrichments can be measured using passive neutron methods. The enrichment of UF_6 is measured by counting neutrons from (α,n) reactions caused by U alpha decay. As the ^{234}U mass fraction grows with increasing ^{235}U enrichment, the (α,n) contribution from ^{234}U increases and the neutron count rate can be used to determine ^{234}U abundances. For low-enriched U (weight percent <5%), the $^{234}U/^{235}U$ ratio is relatively constant. If one can estimate the amount of ^{234}U in a known quantity of UF_6, then one can use the constancy of the $^{234}U/^{235}U$ ratio to obtain an estimate of the ^{235}U enrichment. Above a ^{235}U enrichment of 5%, the $^{234}U/^{235}U$ ratio varies too widely to assume a constant ratio for an unknown sample.

Scope of Applications

Passive neutron counting is routinely used by auditors to verify the enrichment of low-enriched UF_6 in 2.5-ton cylinders and has been used for in-line process monitoring of the ^{235}U enrichment of low-enriched UF_6 in a gaseous diffusion enrichment facility.

Summary of Performance

See Table 5.41 for a performance summary.

Equipment

Portable detector systems have been used for enrichment determination for field measurements. Portable SNAP-II detectors (directionally moderated ^3He counters) are routinely used to measure cylinders containing UF_6. These units are placed in contact with the cylinder wall to minimize the relative magnitude of background neutrons from other cylinders typically present when this measurement is made. Net contact rates of about 5000 counts/min were observed for measurement of a type 30 cylinder containing 5000 lb of UF_6. A SNAP-II detector costs about $6000. More details about the SNAP-II detector can be found in Section 5.2.2.1.

Passive neutron counters have been used for in-line measurements of the ^{235}U enrichment of UF_6 in a gaseous diffusion facility. A bank of moderated ^3He counters monitors the neutron count rate, and the result is transformed into an enrichment for the UF_6 stream passing enroute to a

Table 5.41 Summary of performance: passive neutron enrichment measurement

Sample Type	Isotopic Composition	Sample Size (L)	Container	Standards	Performance (% RSD) Random Error	$\frac{\text{NDA-TAG}}{\text{TAG}}$ x100	Remarks	Ref.
UF_6 in large cylinders	1.3 to 4.0% ^{235}U	736	Gas cylinder	Two cylinders used as standards	1.5	5.6, 6.5	SNAP detector	102, 120 121
UF_6 in piping	2% to 3% ^{235}U	1.6	Steel piping	Material analyzed by mass spectrometry	—	1.3 application	Process control	121 through 124

[a] All data from literature survey.

filling product cylinder. A schematic of this unit is shown in Figure 5.36. A system similar to the one shown costs $35,000.

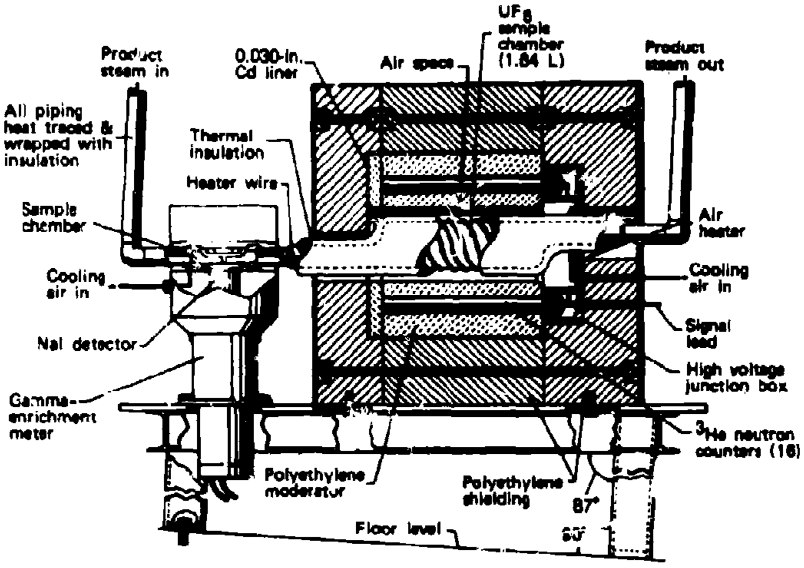

Figure 5.36 UF_6 neutron counter and gamma-ray enrichment meter assembly. (Figure courtesy of Los Alamos National Laboratory.)

Major Sources of Error

Systematic shifts in the $^{234}U/^{235}U$ ratio for a particular ^{235}U enrichment can occur as a result of changes in cascade operating conditions. Because the measurement is based on ^{234}U generated neutrons, this variation will lead to systematic errors in the ^{235}U enrichment results unless frequent recalibrations of the system are made using mass spectrometry. In a 1-month period, the $^{234}U/^{235}U$ ratio was observed to drift over a range of 7%.

Large variations in the amount of UF_6 in the cylinders cause variations in the attenuation of escaping neutrons. Monte Carlo calculations indicated a drop in the fraction of neutrons escaping a cylinder from 0.93 to 0.82 as the UF_6 fill weight was increased from 2000 to 5000 lb for 2.5% enriched ^{235}U (Ref. 120).

Measurement Control Requirements

In using portable NDA equipment, varying environmental, instrumental, and background conditions must be considered. Replicate measurements should be made on a reference source in the course of measuring objects with unknown enrichments or SNM content. At least one measurement should be made before and after a series of assays is performed. For measurements of UF_6 cylinders, repeated measurements could be made on one cylinder chosen as a standard. Neutron measurements for enrichment are usually made in the presence of a measurable neutron background from other UF_6 sources. Background checks should be made frequently if appreciable changes in background levels are encountered or expected.

Data Analysis Requirements

The observed neutron count rate per unit weight of UF_6 can be written as

$$S = a + b'I_{234} \qquad (5-60)$$

and if the $^{234}U/^{235}U$ ratio is constant:

$$S = a + bI_{235} \qquad (5-61)$$

where a, b', and b are constants and I_{234} and I_{235} are enrichments.

In the measurement of UF_6 cylinders, the constant terms a and b can be determined by measuring certain cylinders and using their stated UF_6 weights and enrichments as calibration values. In-line systems are similarly based on mass spectrometric values. The conversion from measured neutron rates to enrichment can be done manually or output directly by system electronics.

Survey of Selected Literature

UF_6, LEU (Refs. 102, 120, and 121)

LEU (1.3% to 4.0% ^{235}U) as UF_6 in the type 30, 2.5-ton cylinders was assayed. A SNAP-II detector and a stabilized electronics package (SAM-I) were used. The detector was placed in contact with the cylinder and counts were taken on both sides of the cylinder for 2 min per side. "Tag" values for enrichment were available and 13 cylinders of two different enrichments were used as standards to determine calibration constants (a and b). The count rate S per pound of UF_6 was related to the ^{235}U enrichment by

$$I_{235} = \frac{S - a}{b} \qquad (5-62)$$

where a = 0.0686 count/(min · lb UF_6) and b = 0.324 count/(min · lb UF_6 × % ^{235}U). The standard deviation of the measured ^{235}U enrichment compared to "tag" values $[(I_{meas} - I_{TAG})/I_{TAG}] \times 100$ was 6.5% for the entire group of cylinders. The measurement precision was 1.5%. The cylinders were in two groups representing UF_6 from two different enrichment facilities. The calibration constants were determined from cylinders from one facility. When the enrichment of the other facility was estimated using these constants, there was a 2.4% bias between the results for each group, which was ascribed to a possible difference in the $^{234}U/^{235}U$ enrichment ratios between the two facilities. A similar variability in $[(I_{meas} - I_{TAG})/I_{TAG}] \times 100$, 5.6%, was reported for SNAP-II measurements of low-enriched UF_6 in another series of field measurements.

UF_6 in a Process Line (Refs. 121 through 124)

The material assayed was UF_6 in a sampling chamber in piping leading to a withdrawal station. The ^{235}U enrichment was 2% to 3.5%.

The neutrons emitted by UF_6 flowing through a sample chamber (volume = 1.6 L) connected to the product withdrawal line from a gaseous diffusion plant cascade was measured. The chamber was surrounded by 16 ^3He proportional counters in a polyethylene moderator and additional shielding. (See Fig. 5.36.) The system was designed to stop UF_6 product withdrawal if the measured enrichment exceeded a preset level. The ^{234}U or ^{235}U enrichment could be measured in 10 min or less.

A NaI enrichment meter (see Section 5.3.1.1) was also used for independent ^{235}U enrichment measurements. Mass spectrometric data for ^{234}U and ^{235}U were available for comparison and calibration. A linear equation was used to relate count rate to ^{235}U (or ^{234}U) abundances.

Twelve ^{234}U determinations from the neutron counter and a mass spectrometer agreed to within 5%. The $^{235}U/^{234}U$ ratio determined from the neutron counter plus enrichment meter measurements agreed with the spectrometer values to within about 5%. For short periods (one week or less), the standard deviation between neutron counter and mass spectrometer values was about 1.3% for the ^{235}U enrichment. This variability was consistent with counting statistics and varying neutron background.

5.4 HOLDUP DETERMINATION

In practice "holdup" means the amount of material that would be left behind if a process stream is emptied in a normal fashion. For example, ductwork as part of a UF_6 process may contain deposits of SNM that remain in place even when the process stream is not running. Similarly, the amount of SNM in U pellets moving through a sintering furnace would not be considered "holdup" but the U dust in the furnace filters would.

Holdup measurements are necessary to determine how much SNM remains in the equipment so the total plant SNM inventory can be determined. Holdup measurements also indicate where concentrations of SNM need to be removed. Of course, it is desirable to keep the amount of SNM in holdup as small as possible.

Holdup determinations can be made with neutron or gamma-ray measurements or both. Generally, gamma-ray techniques are more commonly used. They are used routinely for determining holdup in filters, ductwork, gloveboxes, and other forms of equipment. In some applications, when the self-absorption or attenuation of the characteristic gamma rays is too great, passive neutron techniques have been used. Gamma-ray techniques are discussed in Section 5.4.1, and neutron techniques are discussed in Section 5.4.2.

5.4.1 Holdup Assay With Passive Gamma-Ray Techniques

Description of Method

Gamma-ray holdup measurements differ little, in principle, from other gamma-ray assay techniques. A collimated detector is placed near the object, and the SNM content is determined using characteristic gamma radiation. Either the object is assayed with one count, or segments of it are separately assayed and the results are summed. However, the problems of gamma-ray attenuation and variable spatial location of the SNM are more pronounced in this application than in others. Possible variabilities in both these characteristics must be dealt with to obtain an accurate result.

Before an assay result can be produced, careful consideration of the effect of source dimensions, source self-attenuation, and equipment/container attenuation must be made. Limits to the variation in sample geometry are based on the maximum possible dimensions of the object measured. The magnitude of this effect can be established by measuring a well-characterized source at various extreme positions. Dependence of the assay on the source dimensions can be reduced by moving the detector farther from the source location. Of course, this also lowers the count rate. A limit of error analysis for geometrical uncertainties is given by Reed, Andrews, and Keller (Ref. 125).

Self-attenuation corrections are difficult because they are dependent on the amount of SNM present and on the details of its distribution. A thin layer of U powder will be less attenuating than the same amount of material in a lump.

The container attenuation effect may be calculated if the material form and thickness separating the detector from the source material are known, or by a separate transmission measurement.

The most reliable results are obtained when a physical standard that consists of an identical piece of "cold" hardware with known amounts of

SNM distributed to approximate actual process equipment holdup is synthesized. The least accurate values result from the measurement of items that have dimensions that are large compared with the sample-detector distance, that have possibly high attenuation factors, and about which nothing is known concerning the distribution of SNM inside.

Generally, NaI detectors are used for holdup measurements because of their ruggedness, portability, and low cost relative to Ge detector systems. The high-resolution capabilities of Ge detectors have not been needed because the gamma rays used for assay can be resolved with NaI. For U these are the 186-keV gamma rays from ^{235}U; for Pu the complex of gamma rays from 387 to 414 keV resulting from ^{239}Pu decay can be used.

As with other gamma-ray assay systems, the detector is collimated to view the area of interest. The collimator design is especially important for holdup measurements because the measurements may be made in areas where other sources may be present and could cause a large background.

Descriptions of collimator design, as well as other measurement procedures for certain common varieties of equipment, may be found in the following references:

Type of Equipment	*Reference*
Duct	3, 126, 127, 128
Filter	125, 126, 127
Glovebox	125 128

More detailed discussions of holdup measurements may be found in Regulatory Guides 5.23 and 5.37 (Refs. 129 and 130) and in References 131 and 132. An example of a holdup measurement using the "concentration meter" principle is described in Section 5.2.1.7.

Scope of Applications

Gamma-ray holdup measurements can be made on ductwork, pipes, gloveboxes, filters, and process equipment in general. The attenuation of the gamma-ray flux by the container walls should not be too great for reliable gamma-ray measurements. Holdup measurements are made routinely at facilities that process Pu or HEU.

Summary of Performance

See Table 5.42 for a performance summary.

Equipment

For the equipment used in the measurement of holdup, the emphasis is on physical ruggedness, portability, the ability to output reliable results

Table 5.42 Summary of performance: holdup assay by passive gamma rays (NaI)

SNM	Process	Equipment Measured	SNM Content (NDA Estimate) (g)	Performance	Source[a]	Ref.
HEU, 88 to 93% ^{235}U	Diffusion cascade (shut down)	Pump and converters		detection limit Pumps: 15, and 46 g Converters: 5 and 8 g	L	121
HEU	Fabrication	Duct	134	±44 g (1σ); chemistry: 91 g	L	125
			1195	±279 g (1σ); chemistry: 1159 g		
	Fabrication	Duct, 10 to 30 cm diameter	432[b]	±59 g[c]; recovered: 419 g	L	127
			457[b]	±47 g[c]; recovered: 386 g	L	127
	Fabrication	Filters	519	±126 g; recovered: 247 g	L	127
			166	±38 g; recovered: 106 g	L	127
	Fabrication	Filter/Duct		Random error = 16% RSD	U	
				Systematic error = 23% RSD	U	
Pu	Fabrication	Gloveboxes (3)	75	+14%[d]	L	128
			300	−7%,[d]		
			824	+9%[d]		

[a] L = literature survey; U = users' survey of production facilities.
[b] NDA estimate of material removed.
[c] Includes random and systematic error.
[d] Difference between amount measured by NDA and the amount recovered from the gloveboxes.

under varying environmental conditions, and production of these results within a short counting time. NaI-based systems that meet these requirements are commercially available. (See Fig. 5.30 for a photograph of such a system.) Small NaI crystals, for example, 5-cm diameter by 1-cm thick for 186-keV ^{235}U, and thicker, 5 cm, for 400-keV ^{239}Pu, are adequate. The detector electronics consist of photomultiplier, high-voltage power supply, preamplifier, amplifier, two SCAs, and scaler-timers contained in a portable unit. Because of varying environmental conditions, the overall gain may shift. This variation can be corrected with a stabilization source (^{241}Am) implanted in the crystal. This source provides a monoenergetic peak in the output spectra that is well separated from the assayed spectral region. System electronics can use this reference peak to stabilize the detector gain.

The high sensitivity of NaI to gamma rays allows for short counting times but also makes detector shielding a necessity. The thickness of shielding required depends on the background gamma energy and intensity. However, a thickness of 0.35 cm of Pb is sufficient for the 186-keV ^{235}U assay, and 1.5 cm is sufficient for the ~400-keV ^{239}Pu assay. These thicknesses of Pb correspond to 1.3% and ~2.4 % transmissions, respectively. Shielding should also be placed on the detector face to block out lower energy gamma radiation that serves only to increase the dead time of the system. Thin Cd sheets are customarily used for this purpose. Detector collimation should be designed so that the detector views only the object under consideration. (Details about the collimator design for duct measurements may be found in Ref. 3.)

Major Sources of Error

The major sources of error arise from the uncertainties in the SNM location, the container attenuation, and the self-attenuation. Background from nearby sources of SNM, for example the next section of ductwork in a ductwork survey, can interfere with the assay. As mentioned, directional collimators and shielding are required to reduce this interference.

An additional complication is the contribution of scattered radiation into the SCA window of a NaI system. This scattering can result in too high a measurement value compared to what would be expected from the exponential attenuation predicted from the known absorber thickness. For systems with representative calibration materials, this effect is compensated for, but for equipment that requires the attenuation to be estimated, this "buildup" effect can lead to biased results.

Measurement Control Requirements

Well-characterized reference materials should be used for calibration sources. The self-absorption of the source should not differ appreciably from that expected from the holdup material. Before a holdup survey is performed, calibration constants should be estimated or measured for each different piece of equipment. Where a number of similar items are assayed, for instance a line of identical gloveboxes, the calibration need be done only once.

Changes in gamma-ray attenuation caused by equipment changes require recalibration of the system. If possible, verification of the holdup assay can be made by comparing a recovered amount resulting from a cleanout with the holdup prediction. To monitor for drifts in detector response, a check source mounted on the inside of a collimator plug should be monitored regularly.

Data Analysis Requirements

Two methods for obtaining a calibration factor are as follows:

(1) ***Determination using calculated estimates of the average attenuation of SNM, assuming a particular distribution of SNM.*** These estimates of attenuation can be obtained from a separate transmission measurement or by explicitly calculating the absorption of known thicknesses of hardware material separating the SNM and the detector. The self-attenuation correction may be estimated by assuming that the SNM has a certain configuration, for example, a thin layer of powder distributed over a glovebox or a thick layer of material on the bottom of a pipe. The estimates of attenuation are used in combination with the measured flux of an unshielded calibration source to determine a calibration factor. The calibration factor k is used to relate the net count rate CR to the SNM mass M by the point calibration formula

$$M = \mathrm{CR}\ k(\mathrm{R_m}/\mathrm{R_{CAL}})^2 \tag{5-63}$$

The factor $(\mathrm{R_m}/\mathrm{R_{CAL}})^2$ is used to correct for measurement distances R_m that differ from the calibration source-to-detector distance (R_{CAL}).

(2) ***Determination by the measurement of known amounts of reference material distributed in pieces of hardware identical to that to be assayed.*** This technique is similar to that used in standards-compensated gamma-ray assay of waste and scrap. More accurate results are obtained with this latter procedure. If the reference source is small in comparison with the area assayed, then it should be placed in various locations in the object that represent the expected holdup distribution, and the averaged result should be used.

Survey of Selected Literature

Plutonium in Gloveboxes (Ref. 128)

Plutonium (94% ^{239}Pu, 6% ^{240}Pu) in a wide variety of gloveboxes and storage boxes having sizes ranging from small boxes to large (6.1 by 3.0 by 2.5 m) wood and fiberglass containers was assayed. The boxes contained a wide assortment of equipment, and some were lined with lead.

A 2-in. diameter by 2-in. thick NaI detector with Pb collimator was used. Two SCAs were used, one set for the 375- to 450-keV energy region, and the other set for 500 to 575 keV. The collimator angular response was measured, and the detector was moved to view overlapping sections of equipment. The detector was typically placed about 60 cm from the equipment. Flat Pu sources in the form of 1 ft^2 sheets made of plastic-sealed blotting paper containing dried Pu solutions were used for calibration. Background counting rates were determined either by covering the detector with Pb or by pointing the detector away from the contaminated equipment. Attenuation corrections were estimated for the container walls from their known compositions and thicknesses.

Assays were done before and after cleanout and were compared to a chemical assay of the amount of material removed. The gamma-ray and chemical assays agreed to within 14% (+ 14%, −7%, and + 9%) for the amount of material removed from three different gloveboxes.

Uranium Holdup in Diffusion Plant Equipment (Ref. 121)

HEU (88-93% ^{235}U) located in shutdown process equipment in a gaseous diffusion plant was assayed. A NaI detector, 2 in. in diameter and 0.5 in. thick, was used to detect the 186-keV gamma ray from ^{235}U. The detector and associated electronics were in a portable package. An analyzer window was set on the 186-keV peak and 12-s counts were taken of 288 pieces of equipment. Short counting times were used to assay the maximum number of components. Measurement of about 10% of the highly enriched cascade components by three persons using both this technique and passive neutron measurements required about a week.

A schematic diagram of the equipment and detector is shown in Figure 5.37. The collimated detector viewed compressors and converters at a distance of about 2 m. A thin metal foil of 93% ^{235}U (0.695 g) was used for calibration. The 662-keV gamma rays from a ^{137}Cs source were used for an attenuation correction by putting the source inside dismantled converters and compressors. Design details of the equipment were also used for attenuation corrections. Monte Carlo calculations indicated that scattered gamma rays may actually be counted in the 50-keV wide window set on the 186-keV line. This effect required a 70% reduction in the attenuation correction factor.

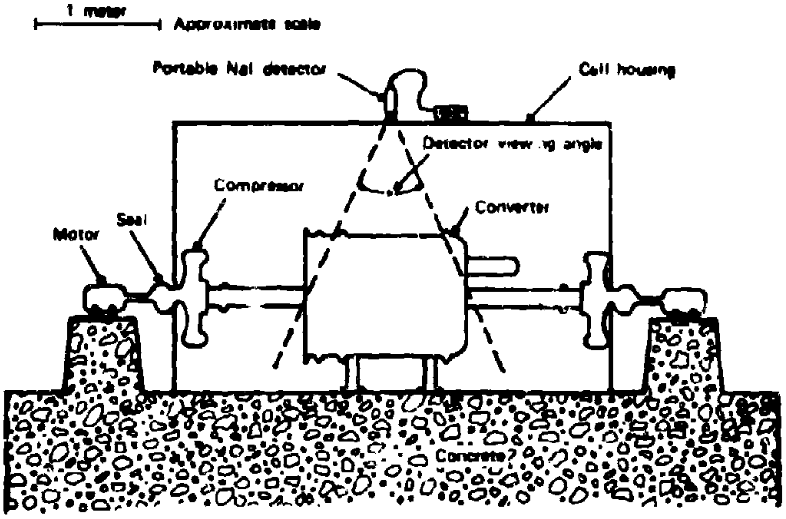

Figure 5.37 Schematic cross section of a cell in a diffusion plant. The detector position used for measuring holdup in converters is also shown. (Ref. 121)

The estimated error in the total inventory of the facility estimated by both passive gamma-ray and neutron methods is about ±50%. Because the equipment was not cleaned out, no independent check of the passive assay could be done. The detection limits at three standard deviations of the background were 15 and 46 g of ^{235}U for the pumps and 5 and 8 g of ^{235}U for the converters for two different areas of the facility, the latter numbers corresponding to larger equipment sizes. The corresponding amounts of ^{235}U per component were 19 and 128 g for pumps and 3.1 and 20 g for converters. The total ^{235}U content of the components measured was 8.2 kg. Extrapolation to all 3500 pumps and converters in the high enrichment portion of the cascade yielded an estimated holdup of 189 kg.

Uranium in Ductwork (Refs. 125 and 127)

HEU plus Th in the ductwork of a fuel fabrication facility was assayed. A 1-in. diameter by 0.5-in. thick NaI detector was used with an SCA. A typical ^{235}U calibration source was in the form of a 90-cm long section of 15- to 20-cm diameter ductwork with 1 to 10 g of ^{235}U distributed evenly on its surface. The assay was corrected for the cylindrical geometry and the presence of Th.

Two sections of ductwork were assayed and then were removed and cleaned out. The contents were assayed. The passive assay results were 134 ± 44 and 1195 ± 279 g of ^{235}U, and the cleanout assay results were 91 and

1159 g of ^{235}U, respectively. The uncertainties given for the passive assays are the results of a limit of error analysis.

In a later study both ductwork and filters were measured using more representative standards and improved NaI instrumentation. Improved accuracy was obtained with the updated system for the duct measurements. Duct surveys before and after a cleanout operation indicated that 432 ± 59 (1σ) g had been removed compared with 419 g actually recovered. For another group of ducts, 457 ± 47 g were determined by the surveys to have been removed compared with 386 g recovered. Similar measurements were made on filter housings containing an intake area, prefilter, and HEPA filters. For this latter case, the amounts recovered were only about 50% of the result determined by the gamma-ray measurement.

Survey of Production Facilities

Holdup determinations of HEU (93% ^{235}U) in (U,Th)O_2 in ductwork and filter housings are routinely made. More than 100 total measurement points are surveyed with a 2-in. by 0.5-in. thick NaI, ^{241}Am-doped (SAM-II) system. Duct reference standards containing 5 to 21 g of ^{235}U are made with U-doped Si rubber deposited on thin vellum paper, which lines the interior of 1.2-m long replicas of 10-, 20-, and 30-cm diameter ductwork. The calibration systematic error is 23%. The random error of the measurement is 16%.

5.4.2 Holdup Assay With Passive Neutron Techniques

Description of Method

Neutrons from SNM spontaneous fission and (α,n) reactions on low-Z elements may be used for holdup assays. The higher penetrability of neutrons through large quantities of metal that often occur in process equipment is a major advantage of neutron assay compared to gamma-ray assay techniques (Section 5.4.1). Neutron assay, however, is complicated by the dependence of the total neutron emission rate on the isotopic and chemical composition of the SNM as was noted in Sections 5.2.2.2 and 5.2.2.3. Coincidence techniques are not applicable because of low counting rates.

This method uses a neutron detector with or without some directional sensitivity, where appropriate. Holdup measurements have been made with ^{3}He proportional counters embedded in moderator material. The same geometrical uncertainties about the location of the SNM as discussed in Subsection 5.4.1 on gamma-ray holdup measurements also occur with neutron assay. More details about holdup determination using passive neutron methods may be found in NRC Regulatory Guide 5.23 (Ref. 129).

Table 5.43 Summary of performance: holdup assay with passive neutron techniques[a]

SNM	Process	Equipment Measured	SNM Content (NDA Estimate)	Performance	Comments	Ref.
HEU, (88% to 93% ^{235}U, assumed to be UO_2F_2)	Diffusion cascade (shutdown)	Seals Seals	Average: 35 and 205 g/seal	65 g at 15 cm detection limit	222 seals measured (SNAP)	121
Pu, (94% ^{239}Pu, 6% ^{240}Pu)	Fabrication	2 gloveboxes	1 kg per glovebox	− 7, − 16[c]	This assay part of larger dismantling and cleanout operation	128
Pu, mixed Pu-U oxide	Fabrication	6 rooms		1.27, 1.5[b]	^{3}He slab detector suspended in middle of room	65

[a] All data from literature survey.

[b] The ratio of holdup determined by neutron and gamma methods. The uncertainty of each method is about 50%.

[c] [(NDA − recovered)/recovered] x 100.

Scope of Applications

This method has had several applications and has been shown to be useful for approximate assay of process plant equipment and total room holdup. This method has been primarily used for the determination of Pu holdup, but has also been used to estimate the ^{235}U holdup in diffusion cascades by detection of ^{234}U-generated (α,n) neutrons from uranium fluoride compounds. It is usually applied only if gamma-ray methods are impractical.

Summary of Performance

See Table 5.43 for a performance summary.

Equipment

The instruments appropriate for this noncoincident neutron counting technique have been described in Section 5.2.2.2. Moderated ^3He proportional counters in various configurations are used for these measurements. A stable high-voltage supply, preamplifier, amplifier, SCA, and timer-scaler are required. Portable electronics packages are available for field measurements. The cost of a neutron assay system suitable for holdup measurements is about $6000.

Sources of Error

The major sources of error are the uncertainty in the location of the SNM and its isotopic and chemical composition. Increased neutron flux from (α,n) reactions not accounted for in the calibration will lead to an overestimate of Pu holdup. Interferences from nearby neutron sources can occur and have to be either estimated through calculations or reduced by use of detectors with directional sensitivity.

Measurement Control Requirements

The stability of portable neutron assay equipment used for determining holdup should be checked regularly using a neutron check source (>100 n/s) such as encapsulated Pu or ^{252}Cf. The check source may be mounted on the inside of a plug of neutron shielding. The instrument stability check can be accomplished by measuring the net count rate from the source before and after a series of holdup measurements. This intensity should fall within set control limits.

Prior to the holdup measurement a check of the area should be made to ensure that no extraneous neutron sources are present that are not part of the holdup. Any physical changes in the equipment being assayed that might affect the neutron intensity reaching the detector will require a new calibration.

If future measurements of the same pieces of equipment are to be made, then the physical location of the detector should be documented. The isotopic and chemical composition of the calibration source should nominally match that of the material assayed. More details on the measurement control requirements may be found in Reference 129.

Data Analysis Requirements

Calibration relating the observed count rate to grams of SNM can be done in two ways. A calibration source that closely matches the material to be assayed may be used to establish the calibration factor, or this factor may be calculated. The calibration factor k is then used to relate the net count rate CR to the SNM mass M by the point calibration formula:

$$M = \mathrm{CR}\, k \qquad (5-63)$$

Calibration using a source is the simpler of the two approaches. The most accurate estimate of the calibration factor would be obtained if a piece of equipment identical to the assayed one could be used. By moving the calibration source into the appropriate spaces where holdup is expected and averaging the results, one could determine the calibration factor.

In some situations it may not be possible to do a source calibration. In that case, the calibration factor may be explicitly calculated using the known masses, geometries, and neutron cross sections of all material that can affect the detector response for a source material of a given composition. Such calculations require the use of neutron transport codes run on large computers. Monte Carlo calculations have been used to estimate the response of a detector to Pu distributed uniformly throughout an entire room (Ref. 65).

Survey of Selected Literature

Uranium Holdup in Diffusion Plant Equipment (Ref. 121)

HEU (88% to 93% ^{235}U) in cleaned out enrichment-plant process equipment (metal seals) was assayed. The chemical form of the U was assumed to be UO_2F_2. The amount of ^{235}U in the seals averaged 35 and 205 g per seal. A schematic of the equipment measured is shown in Figure 5.37.

The measurements were performed with a neutron counter consisting of two 1-in. diameter by 20-in. long ^{3}He counters wrapped in a 1-in. layer of polyethylene clad with Cd. The detector was hand-held and connected to a portable electronics unit. Cylinders containing known weights and isotopic compositions of UF_6 were used to calibrate the detector. A ^{252}Cf source was used for normalization during the measurements. Measurements were performed at 15 or 30 cm from the smaller and larger seals. An (α,n) neutron production ratio was calculated assuming the material to be UO_2F_2 with a $^{235}U/^{234}U$ ratio of 165. The count rates were 0.25 (count/min)/g of ^{235}U at 15 cm and 0.113 (count/min)/g at 30 cm. A counting time of 60 s per seal was used, with longer background counts taken after several seal measurements.

The ^{235}U detection limits, at three standard deviations of the background, are 65 g at 15 cm and 235 g at 30 cm. Of the 2352 seals actually present at portions of the plant, 222 seals were measured. The seals varied in average holdup depending on size. A total of 26 kg ^{235}U was determined to be held up in the components measured, and the estimated total for all seals was 285 kg of ^{235}U, assuming the average values. The estimated error in the total inventory of the facility estimated by both passive gamma-ray and neutron methods is ±50%.

Plutonium in Gloveboxes (Ref. 128)

Plutonium in a large number of gloveboxes and storage boxes having sizes ranging from small boxes to large (6.1 by 3.0 by 2.5 m) wood and fiberglass containers was assayed. The boxes contained a wide assortment of equipment, and some boxes were lined with Pb.

Neutron measurements were used instead of gamma-ray assay (see Section 5.4.1) when the container had shielding materials too thick for a good gamma-ray assay, or if the gamma-ray assay indicated a localized accumulation. A SNAP-II detector (described in Section 5.2.2.2) was used with a portable electronics package. A standard that was similar in isotopic and chemical composition and anticipated total neutron yield to the holdup material was used to calibrate the detector. A point calibration was used. The source-detector distance was the same for the calibrations and the measurements. The angular response of the detector was measured and used to determine how many different placements of the detector were needed to assay a given large container. The detector was calibrated for each sample at the time of assay. Where double-walled storage containers were assayed, the empirical correction was made for the effect of the walls on the neutron flux. Counting times of 2 to 5 min per sample were used.

The neutron assay estimates of the amount of Pu removed were determined by measuring a container before and after cleanout. For two gloveboxes the neutron assay values were low, by 16% and 7%. The amount of Pu assayed and removed was about a kilogram for each glovebox.

Plutonium in Rooms (Ref. 65)

PuO_2 dispersed in six laboratory rooms used for fuel fabrication of MOX fuel pellets was assayed. A quantitative estimate of the amount of

Pu remaining in an entire room after cleanup was desired. The neutron detector consisted of five ^{3}He tubes embedded in a slab of polyethylene and suspended above the floor in the center of the room to be assayed. A portable electronics package was used for counting. The tubes were not shielded with Cd to allow the detector to be sensitive to low-energy scattered neutrons. The detector efficiency was calculated as a function of neutron energy and was found to be constant (±10%) in the energy range from 1.0 ev to 0.5 MeV. Part of the calibration factor relating the response of Pu content was calculated using a Monte Carlo transport code since calibration with a source was not possible.

A gamma-ray survey was also made of each of the rooms, and the result for one room was used as a calibration for the neutron measurements. The material was assumed to be uniformly dispersed in the room. There were no "hot spots" found in any of the rooms; that is, no high concentrations of Pu were found by a hand survey.

Only the material in one room (No. 1) was well characterized. The processes used in room No. 1 was "dry" compared to the "wet" processes in the remainder of the rooms. If the specific neutron activity of the first room were applied to the remainder of the rooms, then the neutron assay for all rooms was a factor of 1.5 times larger than that indicated by a gamma-ray survey that was also performed. The relative difference decreased to 1.27 when the neutron and gamma-ray holdup results were normalized to each other using a "wet" room gamma-ray result as the calibration. One possible explanation of the decreased ratio was that the "wet" room material emitted more neutrons per second per gram than the "dry" room. Both gamma-ray and neutron techniques were estimated to have an accuracy of 50%.

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CHAPTER 6

Active Nondestructive Assay Methods

6.1 INTRODUCTION

Nondestructive assay (NDA) of special nuclear material (SNM) is the determination of the quantity of SNM in a sample from measurements that do not alter the sample in any significant manner. (The term "sample" is used in this chapter for any item being measured.) Passive NDA, described in Chapter 5, is a form of assay in which radioactive decay of the SNM itself provides the basis for measurements. Active NDA, described in this chapter, uses an auxiliary (interrogation) source of neutrons or photons or both to irradiate the sample to induce nuclear reactions, generally fissioning the SNM. The quantity of SNM is determined from measurements, usually counting rates, of neutrons or photons or both which are emitted as a consequence of the fissioning process. Active NDA is a complementary technique to passive NDA, and sometimes both techniques are used to assay a sample.

Active NDA systems have been used to assay SNM in samples ranging from small, well-characterized fuel pellets to 55-gal. (208-L) drums of poorly characterized waste. Some systems have been designed for specific applications, for example, the assay of the ^{235}U content of fuel rods as part of a production sequence. Other systems have been designed to handle samples differing in size and shape and to be capable of assaying different types of SNM.

Chemical assay, described in Chapter 4, is capable of high accuracy, but it suffers from its inability to assay more than a portion of a sample or a product run. When the sample is heterogeneous, unless the whole sample is assayed, an aliquot withdrawn for chemical assay may not be truly representative of the entire sample. With a properly designed active NDA system, however, an entire sample or product run can be assayed. The major advantages of active NDA (as well as passive NDA) over chemical assay are that, following the measurement, the sample is unchanged, additional waste is not generated, and the measurements are more timely.

In Sections 6.1.1 through 6.1.4 some background information designed for the nonspecialist in active NDA is given. Topics include basic nuclear physics concepts, calibration and measurement control, sources of error, and equipment related to active NDA. The reader who is interested

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in a detailed discussion of active NDA principles and applications is referred to *Active Nondestructive Assay of Nuclear Materials* by T. Gozani (Ref. 1). Another basic reference is *The Detection of Fissionable Material by Nondestructive Means* by R. Sher and S. Untermyer II (Ref. 2). Table 6.1 in Section 6.1.5 is a preview of systems and techniques covered in this chapter.

6.1.1 Basic Concepts

The "cross section" for a given nuclear interaction (a specific combination of type and energy of incident radiation, target isotope, and reaction) is a measure of the probability that the interaction will take place. The dimensional unit for cross section is the "barn" and 1 barn is defined as 1×10^{-24} cm^2. The cross sections (Ref. 3) for neutron-induced fission, the (*n*,f) reaction, for ^{235}U and ^{239}Pu are shown in Figure 6.1. Note in this figure that in the energy range from 0.01 eV to 1 MeV each cross section spans about three orders of magnitude, having higher values at lower energies. It can also be seen that the cross sections differ for each isotope. In the 1- to 100-eV region the ^{235}U(*n*,f) cross section shows many maxima and minima with large variations in magnitude. This is the so-called "resonance" region. The ^{239}Pu(*n*,f) cross section also has resonances in this region, but these data have been omitted from the figure for clarity.

Isotopes such as ^{235}U and ^{239}Pu, which readily undergo the (*n*,f) reaction with thermal neutrons, are called "fissile" isotopes. (Thermal neutrons are those in thermal equilibrium with their environment and have an average energy of 0.025 eV.) On the other hand, ^{238}U is not a fissile isotope; its thermal neutron (*n*,f) cross section is less than one millionth that of ^{235}U. It is, however, a "fertile" isotope—an isotope that can become fissile through the process of neutron absorption followed by radioactive decay. In this case the fertile isotope ^{238}U can become the fissile isotope ^{239}Pu. Figure 6.2, which shows the (*n*,f) cross sections (Ref. 3) in the MeV region for ^{235}U, ^{238}U, and ^{239}Pu, illustrates the differences between cross sections for fissile and fertile isotopes. Note, also, that the cross sections for the two fissile isotopes differ in this energy region as well as at lower energies. The ^{238}U(*n*,f) cross section drops to near zero just below 1 MeV, and the energy where this drop occurs is called the "threshold energy" for that reaction. Above the threshold energy, the ^{238}U(*n*,f) cross section is the same order of magnitude as that for ^{235}U(*n*,f). (The term "fissionable" is sometimes used and refers to heavy isotopes that can be fissioned by any means.)

As a result of nuclear fission, neutrons are emitted during the fission process and during radioactive decay of the fission products. Those emitted immediately ($<10^{-14}$ s following fission) are called "prompt" neutrons. Those emitted at a later time are known as "delayed" neutrons. The half-lives of the delayed neutron fission product precursors vary from a fraction of a second to 56 s. The numbers of prompt and delayed neutrons and the time dependence for the emission of each type depend on the particular isotope and the energy of the interrogating neutrons. As an example, when the $^{235}U(n,f)$ reaction occurs with thermal neutrons, an average of 2.4 neutrons are emitted per fission and ≈ 1.6% of these, or 0.038 neutron per fission, are delayed neutrons.

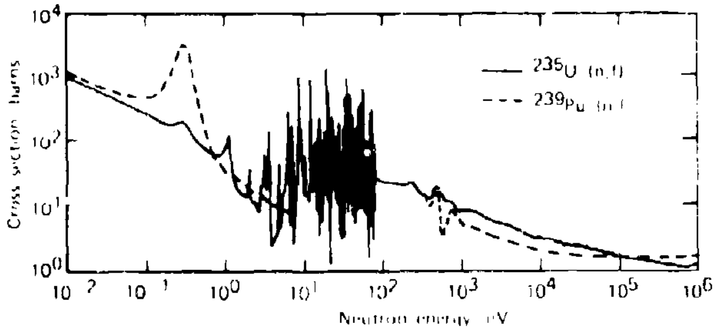

Figure 6.1 The fission cross sections of ^{235}U and ^{239}Pu. (The ^{239}Pu cross section from 6 to 500 eV has not been included.)

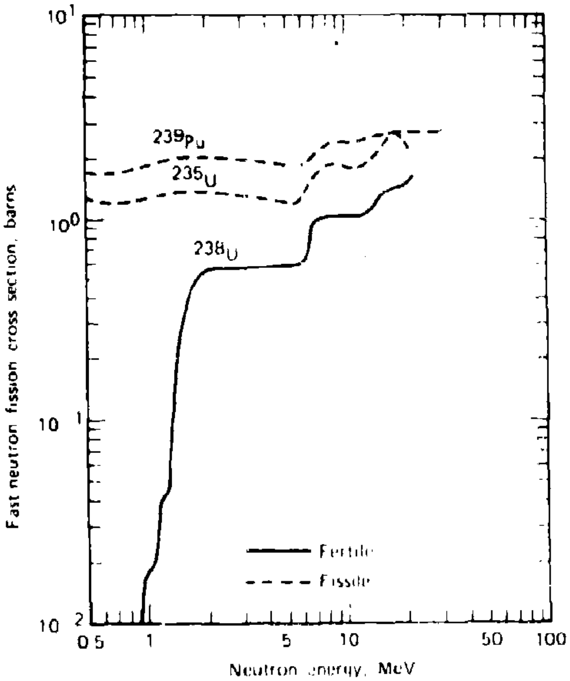

Figure 6.2 The fission cross sections of ^{239}Pu, ^{235}U, and ^{238}U.

Neutrons emitted during the fission process cover a continuous range of energies. The energy distribution of these neutrons is known as a "fission neutron spectrum." Figure 6.3 shows such a spectrum for ^{235}U (Ref. 4). This is the total fission neutron spectrum, but, because the delayed neutron yield is so small, the spectrum is dominated by prompt fission neutrons. Fission neutron spectra for other isotopes have the same general shape. The average energy for the ^{235}U fission neutron spectrum is ≈1.9 MeV, the median energy is ≈1.6 MeV, and the most probable energy is ≈0.65 MeV.

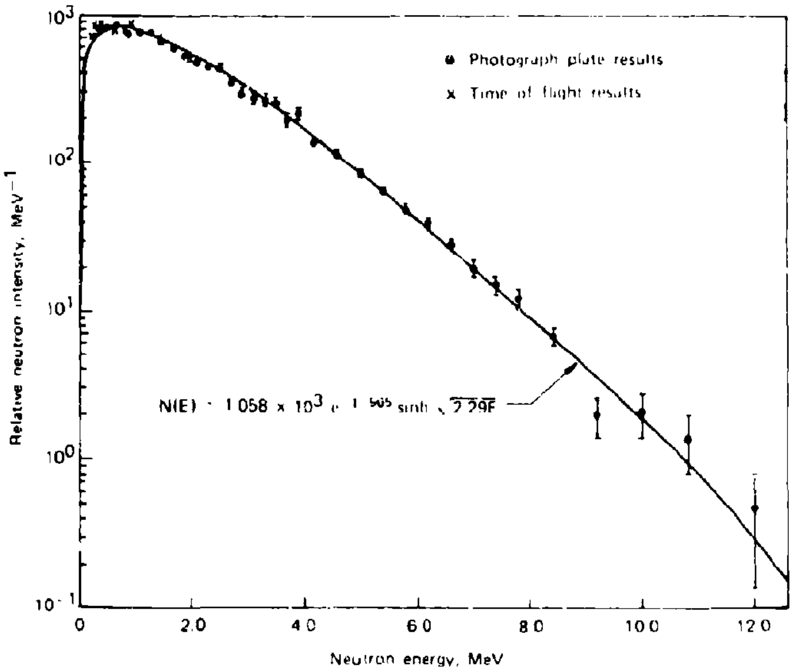

Figure 6.3 Fission neutron spectrum of ^{235}U. The equation shown is one of two types commonly used to describe fission neutron spectra; the other is the Maxwellian, $N(E) = a\sqrt{E}\ e^{-E/T}$. ($a$ = constant; E = kinetic energy; T = nuclear temperature; $N(E)$ = number of neutrons with specific energy E.) For these data T = 1.29 MeV.

Delayed neutrons have less energetic spectra than prompt neutrons with an average energy of ≈0.4 MeV. Figure 6.4 is a delayed neutron spectrum for thermal neutron fission of ^{235}U (Ref. 5). The fine detail shown in this figure is a result of the manner in which the spectrum was obtained.

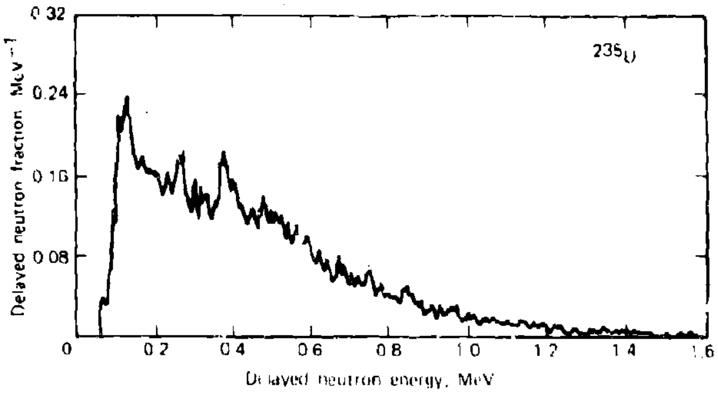

Figure 6.4 Equilibrium delayed neutron spectrum for thermal neutron fission of ^{235}U.

Gamma rays emitted during the fission process are also labeled "prompt" and "delayed," with delayed gamma rays usually understood to be those emitted ≈5 × 10^{-8} or more seconds after fission. During thermal neutron fission of ^{235}U about seven prompt and seven delayed gamma rays in the 0.3 to 10-MeV energy range are emitted per fission. The energy spectra (Ref. 6) of gamma rays for thermal neutron fission of ^{235}U and ^{239}Pu and for spontaneous fission of ^{252}Cf are shown in Figure 6.5.

The radiation emitted in the fission process that is primarily used to determine the quantity of an SNM present is known as "signature" (or "fingerprint") radiation. Some active NDA techniques use only one type of radiation, such as prompt neutrons or delayed gamma rays, for signature radiation while others use more than one.

Frequently the energies of neutrons from the interrogating source or neutrons released in the fission process are not optimum for either initiating the desired fission reaction or for being counted efficiently, respectively. For example, in an application one may want to reduce the energies of interrogation neutrons below the threshold for the ^{238}U(n,f) reaction or to reduce the energies of signature neutrons to the thermal region where they can be efficiently counted with $^{10}BF_3$ or ^{3}He proportional counters. This energy reduction, known as "moderation," occurs as a result of certain reactions that neutrons can undergo as they travel through matter. One such reaction is "elastic scattering." When a neutron is elastically scattered, its energy following the reaction ranges from the incident energy E down to a minimum E' given by

$$E' = E\left[\frac{A-1}{A+1}\right]^2 \qquad (6\text{-}1)$$

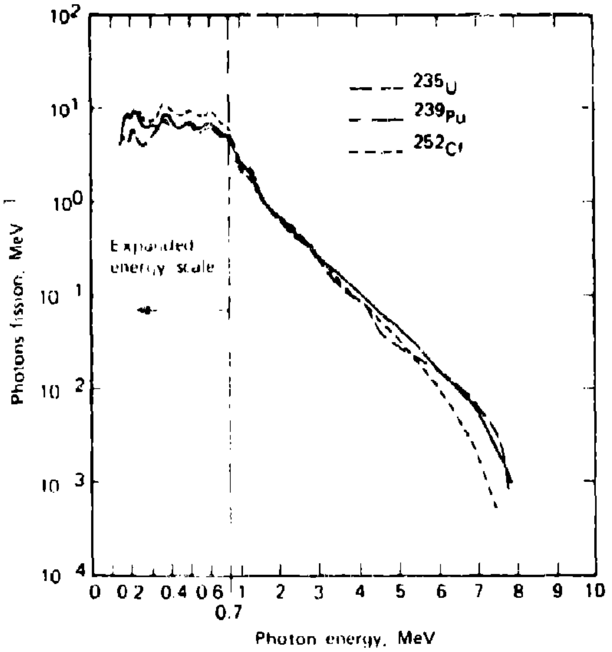

Figure 6.5 Prompt gamma-ray energy spectra for thermal neutron fission of ^{235}U and ^{239}Pu and for spontaneous fission of ^{252}Cf.

where A is the atomic weight of the scatterer. For scattering by hydrogen, $E' = 0$ and the average neutron energy loss per elastic scatter is 50%. As A increases, the average loss in energy per elastic scatter gets smaller. For example, with lead ($A \simeq 207$) it is only 1%. Low atomic weight materials make the best neutron moderators. Hydrogenous materials such as water and polyethylene are often used as moderators.

Another reaction in which a neutron loses energy is "inelastic scattering," a reaction in which part of the energy of the incident neutron is transformed into gamma radiation. This reaction is significant for neutrons with energies in the MeV region when target nuclides have intermediate or high atomic numbers. In the MeV region, the overall energy loss due to inelastic scattering [illegible] be greater than for elastic scattering. Other neutron-induced reactions include (n,γ) in which a neutron is absorbed into a nucleus; $(n, 2n)$, where there is a net gain in the number of neutrons following the reaction; and (n,α) and (n,p) in which charged particles are released. The (n,α) and (n,p) reactions are the neutron-detecting reactions in BF_3 and ^{3}He neutron counters, respectively.

The process of altering a neutron spectrum through the judicious use of different moderating materials such as polyethylene, carbon, tungsten, and lead is called "tailoring." If the resulting spectrum has a lower average energy than the primary spectrum, it is said to be "softer," and if it has a higher average energy, it is "harder." Figure 6.6 shows four curves (Ref. 7) that illustrate the change in delayed neutron response with interrogation energy E_n. One curve is for unmoderated 14-MeV neutrons and three are for moderated 14-MeV neutrons. (Response is a general term used to describe the output of a measuring system; in most active NDA systems, the response will be a counting rate.)

Neutron moderation is not always desirable. For example, the response of a system per unit mass of SNM can be changed by the presence of moderating materials in a sample and sometimes unknowingly. In one

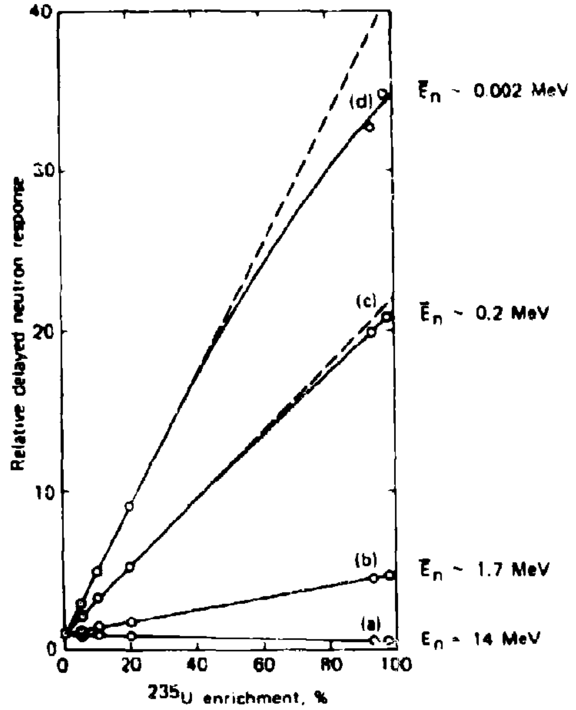

Figure 6.6 Delayed neutron response for samples of U_3O_8 for different enrichments of ^{235}U (total mass of U held constant). Curve (*a*), is for 14-MeV neutron irradiation, and curves (*b*), (*c*), and (*d*) are for moderated 14-MeV neutrons with successively decreasing average energies. The numbers on the right are the mean neutron energies for each moderator. (The dashed lines indicate what curves (*c*) and (*d*) would be if the responses had been linear with enrichment.)

system (Ref. 8) in which delayed neutrons were counted, there was a 1% increase in counting rate for each 10 mg of hydrogen added to the sample. To correct for the hydrogen content of the sample, a detector was added to that system to measure thermal neutrons. The presence of hydrogenous material in samples can be a major source of error for active NDA techniques.

The fact that the energy dependence of the $^{235}U(n,f)$ and $^{238}U(n,f)$ cross sections are so different has led to the "two-spectra" method for simultaneously determining the amounts of both isotopes in a sample. Two measurements of a sample are made with a different interrogation spectrum used for each measurement. This leads to two equations in two unknowns:

$$a_{15}m_5 + a_{18}m_8 = y_1 \tag{6-2}$$

$$a_{25}m_5 + a_{28}m_8 = y_2 \tag{6-3}$$

where

a_{15} = response per unit mass for spectrum 1 to ^{235}U
a_{18} = response per unit mass for spectrum 1 to ^{238}U
a_{25} = response per unit mass for spectrum 2 to ^{235}U
a_{28} = response per unit mass for spectrum 2 to ^{238}U
m_5 = mass of ^{235}U
m_8 = mass of ^{238}U
y_1 = total response for spectrum 1
y_2 = total response for spectrum 2

The equations are solved for m_5 and m_8. Other pairs of isotopes could be assayed in this manner provided the responses for each isotope to each spectrum are sufficiently different.

6.1.2 Calibration and Measurement Control

In all active NDA systems only a fraction of the radiation from the interrogation source reaches the sample, and only a fraction of the sample radiation reaches the detector system. It is impossible to calculate these fractions with sufficient accuracy for most purposes and, hence, the calibration of active NDA systems relies on standards. These standards must be representative of the sample to be assayed. What "representative" means will depend on each active NDA system, the specific sample being assayed, and the accuracy sought. Usually there is a standard or set of standards for each type of sample being assayed. In some cases, such as fuel rod assay, standards that duplicate samples can generally be readily obtained. In other cases, such as 55-gal. drums of waste, available standards may only approximate the sample. When samples are assayed for which there are no good standards, auxiliary measurements may be needed. All standards must be well characterized, and their fissionable material content should be assayed by the best means available.

There are different approaches to obtaining standards. One approach is to select one or more samples that were previously assayed with the active NDA system being calibrated and to assay them by an independent technique. If the independent technique is chemical assay, the sample will be destroyed during the assay, and its unavailability for future measurements may be a disadvantage. An approach that circumvents this disadvantage is to select duplicate sets of samples such that the responses for each set to the NDA system are nearly the same. One set can then be destructively analyzed while the other is retained as a standard. Still another approach is to fabricate standards that closely resemble the samples and contain known amounts of SNM. A disadvantage of this approach is that the standards may not resemble the samples closely enough. An advantage is that the standards are available for additional measurements.

Fabricating representative standards for scrap or waste assay is especially difficult. Standards have been fabricated in two different ways. One way is to place known amounts of SNM in fixed positions in a container together with the matrix materials. The second is to "throw together" the SNM and matrix material in a random fashion. If a large number of standards are randomly made, the mean response for the standards should approach that for the samples. Additional discussion on standards fabrication for NDA is found in Section 5.2.1.2 of this handbook.

A technique that is sometimes used to circumvent the lack of a suitable standard is called "add-a-gram" (Ref. 9). With this technique, the detector response for the sample is determined by counting a sample twice: first, it is counted as it is, and second, it is counted with a known amount of SNM added. The add-a-gram technique can be used only with those samples to which the additional SNM can be added in such a manner that the response per unit mass of SNM following the addition is valid for the unaltered sample.

Calibration should be performed with standards that bracket the amount of SNM expected in the samples. The isotopic composition of fissionable materials in the standards must be similar to that in the samples or the effects of varying the composition must be known. A calibration curve will probably be linear or represented by an exponential equation of the form

$$R = a(1 - e^{-bM}) \tag{6-4}$$

where R is the system response corrected for background effects, M the mass of SNM, and a and b are constants. Figure 6.7 is a plot of this equation. This type of equation is typical when self-attenuation is present. To obtain a calibration curve, ANSI Standard N15.20–75 (Ref. 10) recommends the use of at least one more calibration standard than the number of constants to be fitted. The method of least squares is generally used to solve for the values of the constants.

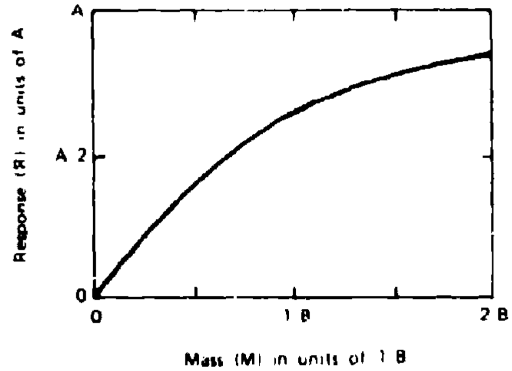

Figure 6.7 A plot of an exponential calibration curve $R = a(1-e^{-bM})$.

Self-attenuation is a significant problem in active NDA. Using a calibration curve that was determined using several standards, each containing a different amount of SNM, is one approach to the problem. Another is to determine the degree of self-shielding with measurements of the sample itself using a technique called the "extrapolated-aliquot method" (Ref. 11). This technique calls for the preparation of a uniformly dispersed sample that can be successively subdivided and diluted. Each aliquot counting rate divided by the mass of the original sample in the aliquot is plotted as a function of the mass of the original sample in the aliquot. The extrapolated intercept for a zero mass gives the counting rate per unit mass of the original sample, corrected for much of the self-shielding effects. This technique is restricted, though, to those samples that can be uniformly separated into smaller samples.

Determination of the quantity of SNM in a sample from a measurement is only a matter of solving the calibration equation for the mass of the SNM. A less precise way would be to read the value directly from the calibration curve. In some instances getting the solution may involve solving more than one equation (e.g., see Equations 6-2 and 6-3). For many active NDA systems all calculations can be readily done with small calculators. For others a programmable calculator or a minicomputer is appropriate. A programmable calculator or minicomputer will be an advantage for systems that have high throughputs. If an accelerator is used as the interrogating source, large amounts of data can be generated, and an automatic data processing system is highly recommended.

The system calibration should be checked, at a minimum, before and after each group of samples is measured. How much time can elapse between these two checks and whether checks should be made during the measurements for a group of samples will be determined by experience. Recalibration will be needed whenever the calibration is suspect or the samples have changed in such a manner that the old calibration is no longer valid. Accurate calibration records are necessary to monitor the performance of an NDA system or set of standards over a period of time.

6.1.3 Sources of Error

Sources of error for active NDA measurements include differences between samples and standards, background radiation, equipment instabilities, and counting statistics.

In active NDA systems, as in passive systems, calibration standards must resemble samples as closely as possible in order that the response per unit mass of SNM for the sample is the same as that predicted by the calibration curve. Several ways in which standards and samples can differ are described in the following paragraphs.

Size, Shape, and Location of the Sample Container and Location of the SNM within the Container. The response is dependent on the relative locations of the interrogation source, SNM, and the detector. In some systems, such as fuel-rod scanners, this "geometry" factor should be easy to control, but in others, such as those used for the assay of 55-gal. drums of waste, it may be hard to control. Rotating the sample and vertical scanning can reduce the geometry error.

Matrix Materials. Materials in the "matrix," the nonfissionable portion of a sample or standard, will result in scattering, moderation, or attenuation of the interrogation and signature radiation. Most important for neutrons are hydrogenous materials because hydrogen is such an excellent neutron moderator. For photons, high atomic number materials such as lead and tungsten are especially significant constituents.

Quantity of SNM. Increasing quantities of SNM can result in self-attenuation, and the response will then be a nonlinear function of the quantity of SNM. (See Figure 6.7.) Multiplication (secondary fissioning initiated by radiation emitted during primary fissioning) can also result as the quantity of SNM is increased. In this case the response would be enhanced.

Fertile Materials. The presence of fertile materials can result in fissioning that is not related to the quantity of SNM. Systems are designed to minimize this effect or account for it by additional measurements. As with all of the previously mentioned factors, it is an unknown change in a sample that can cause problems. For example, an unknown change in the

$^{235}U/^{238}U$ ratio in a system in which both isotopes are fissioned and neither is individually determined will lead to error in the assay.

Material and Thickness of Container Walls. Differences between container walls for samples and standards can result in different degrees of scattering, moderation, or attenuation for interrogation and/or signature radiation and consequently different responses.

All active NDA systems have a counting background that must be subtracted or otherwise accounted for. Contributions to this background include radiation from the interrogation source, radiation from the sample such as neutrons from (α,n) reactions and spontaneous fission, and natural background radiation. In some systems one or two of these background sources might be insignificant in comparison to the others.

Equipment instabilities can affect results, but a thorough knowledge of the equipment and sufficiently frequent stability checks will minimize errors from this source.

Errors from counting statistics can be reduced only by using longer counting times, more intense interrogation radiation, or a more efficient detection system. If the quantity of SNM is small, the total number of counts accumulated may be small and counting statistics can be the dominant source of error. Even in cases where there are large numbers of counts, counting statistics can be a major source of error, if the answer depends on the difference between two large numbers of approximately equal size.

It is important to recognize what is meant when biases are reported in this chapter. Bias represents the difference between two independent measurements of the same quantity. This generally means a comparison between active NDA and chemical assay although in a few cases it is a comparison with calorimetry. Because active NDA techniques depend on standards, any bias statement means a comparison between a result obtained from a previously determined calibration curve for an active NDA system and another anlaysis, for example, by chemistry. The active NDA calibration curve itself may be based on a prior chemistry assay. Any new analysis could, of course, be a recalibration of the active NDA system. Also, in this chapter the word accuracy is used when errors cannot be identified as either random or systematic but some combination of these. The reader is referred to Chapter 2 of this handbook for a more detailed discussion of errors.

6.1.4 Equipment

Active NDA systems consist of some or all of the following components:

(1) Interrogation source with associated shielding, collimation system, and operational controls

(2) Moderating and filtering assembly for neutron spectral tailoring
(3) Sample chamber (possibly equipped for rotation)
(4) Detector assembly including moderators to enhance detection of signature radiation, and filters and shields to inhibit detection of undesired radiation
(5) Electronic circuits for biasing detectors, energy analysis, data processing, and calculations

Interrogation sources fall into two main categories: accelerators and isotopic sources. Positively charged particle accelerators are used as neutron sources for neutron-induced fissioning. They include the relatively inexpensive Cockcroft-Walton type producing 14-MeV neutrons and the more elaborate Van de Graaff type that can produce neutrons in several energy ranges. The electron linear accelerator (LINAC) is used in active NDA as a photon source for photon-induced fissioning. The LINAC is also used as a low-energy neutron source when the photons produced by it strike a target of beryllium or deuterium to produce photoneutrons. Isotopic sources are sealed containers of radioactivity emitting neutrons and photons. Such sources are typically small, with dimensions from less than a centimeter to a few tens of centimeters. Handling isotopic sources requires only minimal training, and such sources require no maintenance other than periodic inspections to ensure the sources are not leaking. Accelerators, on the other hand, are considerably larger, sometimes requiring a separate room, and need a trained operator. Because accelerators are high-voltage electrical machines, trained personnel are required for maintenance. Both accelerators and isotopic sources require shielding and radiation monitoring for personnel protection. The amount of shielding required will depend on the radiation levels.

Another type of source, which has received only limited use in active NDA, is the nuclear reactor. Suitable reactors require provision for either moving the sample into the neutron radiation field in or near the reactor core or extracting a neutron beam from the reactor for irradiation.

The spectrum tailoring assembly is usually a composite consisting of concentric cylinders of various materials such as lead, tungsten, carbon, or polyethylene surrounding the source or the accelerator target. Typical diameters of tailoring systems are 6 to 15 cm. Various combinations will produce different spectra with different mean energies and neutron leakage. Neutron leakage is the number of neutrons, of all energies, that escape in all directions from the spectrum tailoring assembly. Only the fraction of these neutrons escaping in the direction of the sample is available for interrogation. The total leakage is usually expressed as a percentage of the number of source neutrons. In one system (Ref. 12) with a 14-MeV neutron source, neutrons moderated by a lead, carbon, and polyethylene moderator assembly have a median energy of 470 keV and a total leakage of 140%. (The leakage is greater than 100% because of the contribution of the (*n*,2*n*) reaction in lead at higher neutron energies.) About 66% of the neutrons have energies less than the fission threshold of ^{238}U, leading to a ^{235}U/^{238}U fission ratio of approximately 300.

The sample chamber in some systems is such that only a single or limited number of sample sizes and shapes can be accommodated, and in other systems the range is quite broad. For highest efficiency, the source and detector should be as close to the sample as is practicable. Some devices provide a means for moving the source and detectors to accommodate different sample sizes. Medium and large samples are usually rotated during the measurement to average the effects of a radial inhomogenous distribution of material. Large sample containers (e.g., 55-gal. drums) are often scanned vertically to reduce the geometry error.

The selection of the detector depends not only on the signature radiation but also on other radiations present. When fission neutrons are to be counted, if there are no interfering neutrons and the gamma radiation level is less than 10 R/h, then a thermal neutron detector such as a BF_3 or ^{3}He proportional counter might be best. A commonly used neutron detector system employing either BF_3 or ^{3}He counters is the "slab" detector (Ref. 13) shown in Figure 6.8. This detector is designed for high efficiency (approximately 10%) and to respond reasonably uniformly to neutrons of different energies. To count thermal neutrons the presence of a very high gamma-ray field, a thermal neutron fission chamber with a ^{235}U converter foil might be the choice.

If fission neutrons are to be counted in the presence of lower energy interrogation neutrons, a threshold detector would be the choice. Such a detector is one which is relatively insensitive to lower energy interrogation neutrons in comparison to higher energy signature neutrons. In one type of threshold detector, the ^{4}He proportional counter, the neutron detection reaction is the elastic scattering by helium. This detector is useable in gamma-ray fields of less than 100 mR/h. Another type is the fission chamber where detection is by the (*n*,f) reaction with a fertile isotope.

When organic scintillators are used as detectors in fast coincidence detection systems both neutrons and gamma rays are counted. In some organic scintillators the life time of the light pulses from neutrons is longer than it is from gamma rays. This has led to the development of pulse shape discrimination circuits for counting neutrons in the presence of low levels of gamma radiation.

If only gamma rays are to be counted, sodium iodide (NaI) crystals are frequently used. However, NaI detectors are useful only up to approximately 2 to 3 × 10^5 counts/s. At higher counting rates, an organic scintillator is used or NaI is operated in the current mode; i.e., the instantaneous current is measured rather than the individual pulses counted. In the current mode, energy (pulse height) information is lost, and, consequently, the ability to discriminate against a lower energy gamma-ray

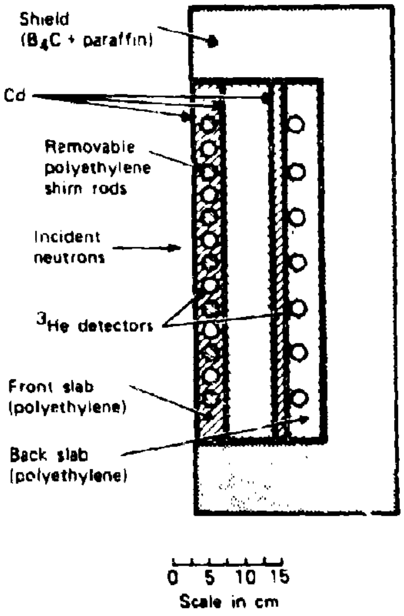

Figure 6.8 Cross-sectional view of a ^{3}He "slab" detector. This configuration is used to obtain coarse neutron energy spectrum information. In the flat-response mode of operation, all materials between the front and back counter banks are removed.

background is also lost. Thus the current mode may not be suitable when significant background is present.

In all cases where neutrons are being counted, high gamma-ray levels can be reduced by using lead shields. Fortunately lead is quite transparent to neutrons.

The electronic setup for a counting system is usually straightforward, and components are commercially available. A typical setup consists of one or more detectors and preamplifiers, a high-voltage supply, amplifier, discriminator, scaler, and printer. Figure 6.9 shows a schematic of a counting system with two detectors in parallel feeding a common preamplifier. One frequent change to the Figure 6.9 system is the substitution of a multichannel pulse height analyzer for the discriminator, scaler, and timer. Another is the substitution of some data processing equipment for the printer.

Some active NDA systems are based on coincidence counting to reduce the background from unwanted radiations. A basic coincidence system is shown in Figure 6.10. The coincidence unit transmits a pulse to

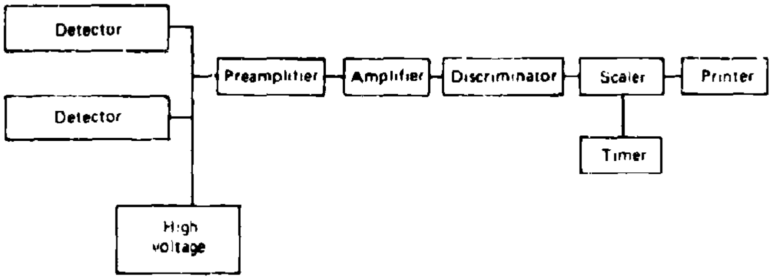

Figure 6.9 A counting system with two detectors connected in parallel.

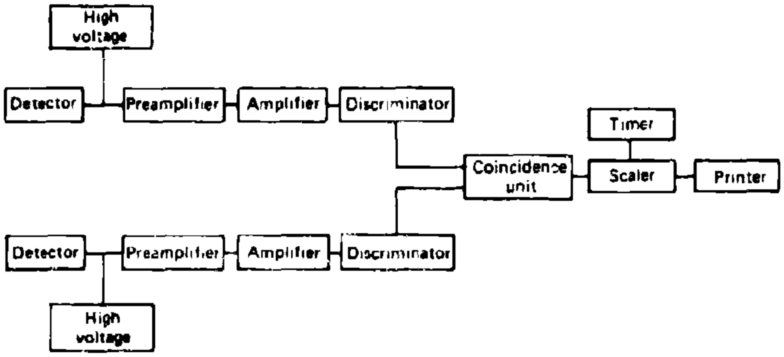

Figure 6.10 A two-detector coincidence counting system.

the scaler when a signal from one detector arrives within a specified time interval after the signal from the other detector arrived. The system is classified as either "fast" or "slow" depending on the length of this time interval. In fast systems this time interval may be about 5 to 100 ns and in slow systms about 16 to 128 μs.

Another way to determine the coincidence counting rate for a slow coincidence system, other than the use of a circuit such as shown in Figure 6.10, is the shift register (or correlated count) concept. This concept is particularly suitable for high counting rate applications and is described briefly in Section 5.2.3.3 of this handbook.

No special requirements are needed for stable operation of electronic equipment in the normal laboratory working environment except for adequate cooling. If several proportional counters are operated in parallel and connected in a common junction box, it may be necessary to ensure that leakage current from the high-voltage connecters is not excessive. If electrical noise (e.g., from heavy electrical equipment such as welders) is present on the power lines, an rf line filter will be needed.

6.1.5 Chapter Preview

The active NDA techniques to be described in this chapter are listed in Table 6.1. When isotopic discrimination is possible, the letter X has been placed in the "Two-Spectra" column. In the last column, samples are identified by size designators S, M, and L and by type designator F. Designator S refers to a small container such as a 15-cm^3 (4-dram) vial, M refers to small or medium containers up to 5 gal. (19 L), and L refers to those containers up to 55 or 80 gal. (208 or 303 L). Type designator F refers to those systems specifically designed for fuel rods. A word of caution: in many chapter sections with an S, M, or L size designation in Table 6.1 the systems described were designed for specific assay problems.

Techniques applicable to one fissile isotope are generally applicable to others. The same is true for fertile isotopes. When isotopic discrimination is possible this generally implies discrimination between fissile and fertile isotopes of the same element (e.g., ^{235}U and ^{238}U), but not always. Isotopic discrimination is possible, though not necessarily done, when an accelerator or isotopic source such as ^{252}Cf or ^{241}Am-Be(α,n) is used. The necessary spectrum modification can be done by tailoring or, in the case of some accelerators, by proper selection of the neutron-producing target, operating voltage, or both.

For the quantitative determination of SNM by active NDA, most techniques depend on fissioning of the SNM. If the signature radiation is delayed neutrons or gamma rays, interrogation radiation must be absent or greatly reduced during the time when signature radiation is measured. For accelerator systems this is accomplished by turning the accelerator beam off. When the interrogating source is an isotopic source, either it or the sample is moved to reduce the interference.

Because of the high gamma-radiation levels associated with irradiated fuel, techniques that rely on prompt or delayed gamma rays for signature radiation cannot be used. Irradiated fuel can be assayed using neutron techniques.

6.2 DELAYED NEUTRON TECHNIQUES

In the design of any active NDA system, the potential interference with the signature radiation by radiation from the interrogating source must be considered. Because some neutrons released in the fissioning process are delayed, interference by the interrogating radiation can be eliminated by using these delayed neutrons as signature radiation and turning off the interrogating source or physically separating it from the

Table 6.1 A preview of techniques included in this chapter

Chapter Section	Interrogation Source/Technique	Principal Signature Radiation	Detector Type	Two Spectra	Sample Size/Type
6.2.1	14-MeV generator; delayed neutron	n_d	n_{th}	X	L
6.2.2	Van de Graaff generator; delayed neutron	n_d	n_{th}	X	L
6.2.3	^{252}Cf; step irradiation; delayed neutron	n_d	n_{th}	X	L[a]
6.2.4	Thermal reactor; delayed neutron	n_d	n_{th}	X	S
6.3.1	Isotopic photoneutron; subthreshold energy	n_p	n_f		M
6.3.2	Sb-Be photoneutron; Fermi age	n_p	n_{th}		M
6.3.3	^{252}Cf; moderated to subthreshold energy	n_p	n_f	X	F
6.4.1	Li(α,n) or ^{252}Cf; fast coincidence systems	n_p, γ_p, γ_d	C	X	L
6.4.2	^{241}Am-Li(α,n); active well coincidence counter	n_p	n_{th}		M
6.5.1	^{252}Cf; fuel-rod scanner	γ_d, n_p	NaI, n_f		F
6.5.2	^{252}Cf; small sample assay system	γ_d	NaI	X	S
6.6.1	LINAC; photofission	n_p, n_d	n_{th}	X	L
6.6.2	LINAC; photoneutron	n_p	n_{th}	X	L
6.7.1	14-MeV generator; Pb slowing down spectrometer	n_p	n_f, n_{th}, C	X	S
6.7.2	Reactor reactivity		(b)	X	S, F
6.7.3	Neutron resonance		(c)	X	S

C = organic scintillator
F = fuel-rod system
L = large sample
M = medium sample
S = small sample
n_d = delayed fission neutrons

n_p = prompt fission neutrons
n_f = fast neutron detector (e.g., ^{4}He proportional counter or threshold fission detector)
n_{th} = thermal neutron detector (e.g., BF$_3$ or ^{3}He proportional counter)
γ_d = delayed fission gamma rays
γ_p = prompt fission gamma rays

[a] If the ^{252}Cf source is moved, all sample sizes up to large may be assayed; if, however, the sample is moved, then only small samples may be assayed.

[b] Control rod position is measured.

[c] Transmission of neutron interrogation radiation is measured.

sample prior to measuring the signature radiation. Both techniques are used. If the interrogating source is an accelerator, it is used in a pulsed mode, and if the interrogating source is an isotopic source, then either the source or the sample is physically relocated. Because the characteristics of delayed neutron emission are not the same for each fissionable isotope, it is also possible, with pairs of measurements, to assay for two isotopes simultaneously.

Delayed neutrons are those neutrons released during radioactive beta decay of fission products, and constitute only a few percent of all neutrons released during fissioning. Delayed neutron yields are functions of the particular fissioning isotope and of the energy of the interrogating radiation. Table 6.2 shows some delayed neutron yields for fissioning induced by thermal and fast neutrons.

Table 6.2 Absolute delayed neutron yields per thermal- and fast-neutron-induced fission of pure isotopes

Isotope	Thermal (*n*/fission)	Fast (*n*/fission)
^{233}U	0.00664 ± 0.00018	0.00729 ± 0.00019
^{235}U	0.01654 ± 0.00042	0.01714 ± 0.00022
^{238}U	—	0.04510 ± 0.00061
^{238}Pu	—	0.00456 ± 0.00051
^{239}Pu	0.00624 ± 0.00024	0.00664 ± 0.00013
^{240}Pu	—	0.0096 ± 0.0011
^{241}Pu	0.0156 ± 0.0016	0.0163 ± 0.0016

Source: Ref. 14.

The delayed neutron precursors are divided into six groups according to their half-lives. The average half-lives of the delayed neutron groups for thermal neutron fission of ^{235}U are as follows (Ref. 14):

Group	Half-Life (s)
1	54.6 ± 1.3
2	21.9 ± 0.8
3	6.0 ± 0.2
4	2.2 ± 0.1
5	0.50 ± 0.04
6	0.18 ± 0.03

Within experimental error, the group half-lives for other isotopes are the same as for ^{235}U. The delayed neutron group yields, however, do vary significantly from isotope to isotope. This is illustrated in Table 6.3 for fast neutron fission of several isotopes. In principle, these time profiles could be used to determine isotopic composition as well as content but, thus far, only limited work has been done using this concept.

Table 6.3 Fractional delayed neutron group yields from fast-neutron-induced fission

Group	^{233}U	^{235}U	^{238}U	^{239}Pu
1	0.086 ± 0.004	0.038 ± 0.004	0.013 ± 0.001	0.038 ± 0.004
2	0.274 ± 0.007	0.213 ± 0.007	0.137 ± 0.003	0.280 ± 0.006
3	0.227 ± 0.052	0.188 ± 0.024	0.162 ± 0.030	0.216 ± 0.027
4	0.317 ± 0.016	0.407 ± 0.010	0.388 ± 0.018	0.328 ± 0.015
5	0.073 ± 0.021	0.128 ± 0.012	0.225 ± 0.019	0.103 ± 0.013
6	0.023 ± 0.010	0.026 ± 0.004	0.075 ± 0.007	0.035 ± 0.007

Source: Ref. 14.

6.2.1 14-MeV Generators

Description of Method

High-intensity beams of 14-MeV neutrons for interrogation can be produced rather inexpensively with small, low-voltage (typically 150-kV) Cockcroft-Walton-type accelerators by bombarding a tritium-containing target with deuterium ions: the T(d,n)^{4}He reaction. To avoid counting interference from the interrogating neutrons, the generator is operated in the pulsed mode. In most systems, the total delayed neutron yield is used for the signature radiation. In a few instances the time profile of the decaying delayed neutron population is used (Ref. 15).

Scope of Applications

This method can be used to assay for fissile and fertile isotopes and to determine enrichment. Virtually the full range of materials, from fuel pellets to waste, has been or can be measured using this technique. Because 14-MeV neutrons can easily penetrate most materials, including hydrogenous substances, the method is particularly suited for measuring large volume containers, including 55-gal. drums containing waste. Because lead is quite transparent to 14-MeV neutrons, the method is also applicable to measuring the contents of irradiated fuel elements in thick lead casks.

Summary of Performance

Results obtained when using this technique depend strongly on the sample size and composition. Errors reported for applications are summarized in Table 6.4; they vary from 1% for well-characterized samples to 36% for waste in 55-gal. drums.

Table 6.4 Summary of performance for 14-MeV delayed neutron technique[a,b]

Sample	Assay Time (min)	Random Error (%)	Accuracy (%)
LEU U_3O_8 scrap (>80% U) and LEU incinerator ash (<30% U); 0.1 to 15 kg of U per sample:			
Total U assay	5	10	—
^{235}U enrichment	10	12	—
Verification samples; subgram to gram quantities of ^{235}U per sample	—	3	—
LEU UO_2 powder samples; 50 mg ^{235}U per sample	—	—	3 (bias)
LEU and HEU uranium oxide and ZrO_2 powders, pellets, and scrap; 1.4 to 3.6 g uranium oxide per sample:			
Total U assay	—	—	1.3
^{235}U enrichment	—	—	1.6
HEU UAl_x powder in 1-gal. cans; 320-kg lot	3	—	0.2 ± 0.95 (for lot total)
Cold material test reactor (MTR) fuel element	20	—	1
Hot MTR fuel element in a 5000-lb lead cask	20	—	2
Fast flux test facility (FFTF)	—	—	^{235}U: 0.6
pellets	—	—	^{239}Pu: 1.4
Pu scrap and waste standards; several wet and dry matrices in 55-gal. drums	—	—	36
Pu waste (heterogeneous matrix) in 1-gal. cans	—	—	8
Pu waste (homogeneous matrix) in 1-gal. cans	—	—	3

[a] Unless otherwise indicated, errors shown are for the determination of the quantity of U or Pu.

[b] No data in this table are from the Users' Survey of Production Facilities.

Equipment

There are two types of commercially available Cockcroft-Walton 14-MeV neutron generators. One type employs a sealed assembly that contains the tritium target. The other, less compact than the former, uses a drift tube and replaceable tritium targets. The sealed tube generally can be used for a few hundred hours before its neutron output has decreased to 50% of its initial yield. A replacement sealed tube costs several thousand dollars. In the drift tube type only the tritium target (at a cost of about

$100) has to be replaced after about 10 h of operation. During replacement, a target with several curies of tritium is handled in the open; this requires special precautions and monitoring equipment. Some 14-MeV systems employ multiple rotating targets to reduce system downtime.

Figure 6.11 shows a schematic of an experimental setup. The spectrum tailoring assembly would be used if it were desired to interrogate the sample with neutron energies other than 14 MeV. The sample (barrel) would probably be rotated about its cylindrical axis during the measurement. The "slab" neutron detector is the primary signature radiation detector. A ^{238}U fission counter monitors the interrogation source intensity. The ^{235}U fission counter, essentially a thermal neutron detector, is used to obtain an estimate of neutron moderation by the sample so that slab detector results can be corrected for this effect. Because this is a pulsed system, the counting circuits need to be off when the generator is on, and turned on by the generator control circuit after the generator is turned off.

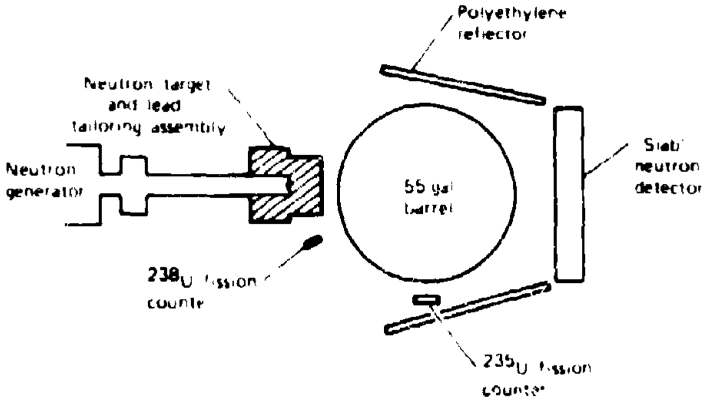

Figure 6.11 Schematic of experimental arrangement for the assay of 55-gal barrels.

Special requirements for a 14-MeV system include adequate shielding for personnel protection and a cooling system for target cooling. The minimum space required for a 14-MeV delayed neutron system is a room of about 9 by 9 by 9 ft excluding the shielding. Often the shielding is built into the walls. A rough cost breakdown of a 14-MeV delayed-neutron system is as follows:

14-MeV neutron generator	$65,000
Tailoring assemblies	15,000
"Slab" detector and electronics	45,000
Shielding, assembly, and miscellaneous	35,000
	$160,000

Major Sources of Error

Measurement errors associated with the 14-MeV delayed neutron technique are those common to most active NDA systems and were discussed in Section 6.1.3. Of special concern, though, is the measurement of samples that have poorly defined matrix compositions. The presence of hydrogenous material, especially, will result in moderation and attenuation of the interrogation and signature beams and, unless accounted for, can lead to errors. The unexpected presence of fissionable material other than that being assayed can also lead to serious errors. For large volume samples with small amounts of SNM, counting statistics will be a major source of error. A potential source of error related to the neutron generator is the variation in the intensity of the interrogating neutron beam which is not adequately compensated for the beam monitor.

Measurement Control Requirements

System calibration for this technique requires the use of standards that closely resemble the samples being assayed. See Sections 6.1.2 and 6.1.3 for discussions of this topic.

Data Analysis Requirements

Data analysis is straightforward and can be done with a small calculator. Use of a programmable calculator may make the process easier and less subject to human error.

Survey of Selected Literature

Uranium and Plutonium Assay in a Mobile Laboratory (Refs. 16 and 17)

Uranium and Pu in scrap and waste were assayed in containers varying in size from 1 to 55 gal. Each container typically contained from hundreds of grams to kilogram quantities of SNM.

The Mobile Nondestructive Assay Laboratory (MONAL), designed and built by Los Alamos National Laboratory, is housed in a 50-ft trailer. In addition to the active NDA system based on a 14-MeV generator, the facility contains a number of passive NDA instruments. The 14-MeV neutron generator delivers 2.5×10^{11} n/s and is located in the rear of the trailer. The assay chamber is 4 by 6 ft and is equipped with an elevator and turntable. Lead is used for spectrum tailoring when 55-gal. drums are assayed. A lead-carbon spectrum tailoring combination is used for small samples. When enrichment is determined with the two-spectra assay method, a tungsten-lead tailoring unit is used for the subthreshold measurement. A "slab" neutron detector is used to count delayed neutrons.

Typical assay results for U_3O_8 scrap containing more than 80% U and incinerator ash with less than 30% U are shown in Figures 6.12 and 6.13. Figure 6.12 shows the assay results for total U content. Each measurement took about 5 min. Figure 6.13 shows the results from a two-spectra determination of isotopic enrichments. Isotopic enrichment determinations required approximately twice the time required for total U assay. The standard deviation of a single measurement for the total U assay was 10% and

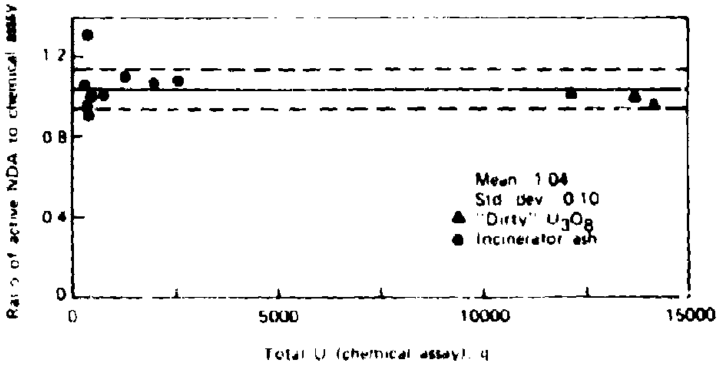

Figure 6.12 Active neutron interrogation results for cans of scrap and ash. The material was subsequently blended and reanalyzed by chemical assay.

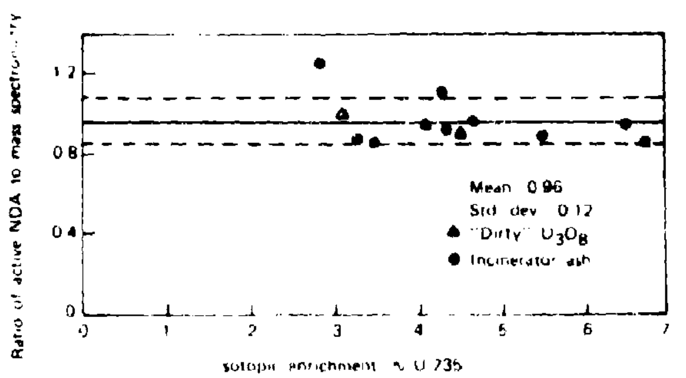

Figure 6.13 Active neutron interrogation results for cans of scrap using the two-spectra method. The material was subsequently blended and reanalyzed by mass spectrometry.

for the enrichment was 12%. The total U assay showed an average difference from chemical assay of +4% and the enrichment determination showed an average difference from mass spectrometry of −4%.

Figure 6.14 shows the results of an assay of 55-gal. drums containing Pu. The random error over this wide range of matrices is ±36%. This error is larger than that for U assay primarily because of the large sample containers, the lower yield of delayed neutrons from Pu, and a high background from ^{240}Pu spontaneous fission neutrons. If representative standards were used for each matrix type, the accuracy would be greatly improved.

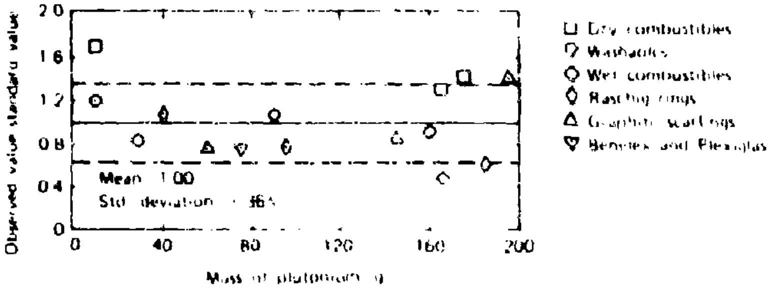

Figure 6.14 Assay results of Rocky Flats 55-gal. drum standards.

Uranium Assay in a Permanent Laboratory (Refs. 15, 18, 19, and 20)

The following were assayed using the 14-MeV, delayed neutron method: intermediate product cans of UAl_x with ^{235}U enrichment of 93%; inventory verification samples containing subgram to gram amounts of ^{235}U; low enriched UO_2 powder samples generally containing less than 50 mg of ^{235}U; powder, pellets, and scrap samples of uranium oxide plus ZrO_2 containing approximately 1.5 g of U each, with enrichments varying from 4% to 98%; and irradiated high-temperature reactor (HTR) fuel elements that consist of graphite, ^{233}Th, ^{233}U, and ^{235}U.

This method was used to determine shipper/receiver differences for 90 cans containing a total of 320 kg of high enriched UAl_x powder. Each can required 3 min to assay. The difference for the total shipment was 0.2% ± 0.95% (1σ). Subsequently, several cans were subjected to chemical analysis. The difference between active NDA and chemical assay was 0.1%. The high accuracy of the measurement was the result of the uniformity of the samples and containers (Ref. 18).

The measurements of 144 inventory verification samples containing from subgram to gram amounts of ^{235}U were compared to chemical assay. The results showed a bias of −3% and a random error from counting statistics of 3% (Ref. 18).

Thirty-nine low enriched UO_2 powder samples, most containing less than 50 mg of ^{235}U, were assayed. A bias of 3% was observed, and the random error was consistent with counting statistics (Ref. 18).

Eight samples were assayed for total U using the two-spectra method. These samples were powders, pellets, and scrap, each containing from 1.4 to 3.6 g of uranium oxide (UO_2, UO_3, and/or U_3O_8) with enrichments varying from 4% to 98%; four of the samples also contained ZrO_2. Subsequently, the samples were subjected to chemical assay. The average difference per sample between active NDA and chemical assay was 1.3% for total U and 1.6% for enrichment (Ref. 19).

The method proposed in Reference 15 for assaying ^{233}U and ^{235}U in irradiated HTR fuel elements (spheres) uses the different delayed neutron time profiles for these two isotopes (Ref. 20 and Table 6.3). It is estimated that the total fissile content of a batch of about 20 spheres could be determined with an accuracy of about 1% and the $^{233}U/^{235}U$ ratio with an accuracy of a few percent.

6.2.2 Van de Graaff

Description of Method

The Van de Graaff accelerator has been used in the assay of SNM. It is a more versatile machine than a Cockcroft-Walton accelerator, but it is also larger and more expensive. An advantage of the Van de Graaff over the Cockcroft-Walton accelerator is that neutrons can be produced in any of several energy intervals to avoid interferences. Thus it is possible, without resorting to tailoring systems, to produce neutrons that are either below or above a specific energy such as the fission threshold of ^{238}U. The Van de Graaff accelerator is operated as a pulsed neutron source when delayed neutrons are used as the signature radiation.

Scope of Applications

The only Van de Graaff assay system operating is at the Los Alamos National Laboratory (Refs. 8 and 21), and it is used mainly to analyze small samples containing up to 10 g of fissile material. In principle, however, delayed (and prompt) neutron techniques based on the Van de Graaff accelerator can be used with all sample sizes and material types, for example, U and Pu in solid and liquid forms and waste and scrape materials.

Summary of Performance

Accuracies obtained for small samples containing from 50 mg to 10 g of U with enrichments varying from 0.7% to 93% ^{235}U are comparable to chemical assay. With care in reducing the background, as little as 5 mg can be detected. Random errors range from 0.6% to 3% RSD. For larger samples, the accuracies will be of the same magnitude as those obtained with the 14-MeV source technique. Table 6.5 provides a summary of pulsed Van de Graaff system performance.

Table 6.5 Summary of performance for Van de Graaff delayed neutron technique[a]

Sample	Assay Time (min)	Random Error (%)	Systematic Error (%)	Accuracy (%)
Mockup of boiling water reactor (BWR) fuel	—	—	—	6
HEU U_3O_8 process residue in a 3-dram vial	—	1 to 2	—	3
2 kg of U_3O_8 in an 18-cm diameter can	1	—	—	2.6
New Brunswick Laboratory laboratory standards[b]	—	0.7	2	—
HEU high-temperature gas reactor (HTGR) microspheres	7	0.67	—	—
Rover HEU inventory verification samples[c]	2	2.4	0.34	—

[a] No data in this table are from the users' survey of production facilities.

[b] Errors shown are for a comparison between passive NDA (gamma rays) and Van de Graaff results.

[c] Errors shown are for a comparison between chemical assay and Van de Graaff results.

Equipment

The Van de Graaff accelerator uses (p,n) or (d,n) reactions to produce neutrons. Target materials include ^2H, ^3H, ^7Li, Be, Sc, and V. Neutrons from the $^7Li(p,n)$ reaction, for example, have energies in the 200- to 600-keV range and can be produced with an intensity of 10^9 to 10^{11} n/s. Higher energy neutrons with higher intensities are obtainable with a tritium target. The accelerator can be operated either continuously or in a pulsed mode. In pulsed operation, on/off neutron flux ratios of 10^9 are obtained, which ensures a low neutron background from the accelerator during the delayed neutron measurements. The detector employed for the delayed neutron measurements should have high efficiency to compensate for the small delayed neutron yields. Los Alamos National Laboratory uses a 13-tube ^3He slab detector. On two sides of the target-sample region (see Figure 6.15) are nickel reflectors designed to make the flux more uniform and to increase the flux in the region of the sample. The sample is surrounded by cadmium shielding to absorb thermal neutrons. Fission chambers are placed on both sides of the sample to correct for variations in the interrogating flux and multiplication in the sample. A measurement

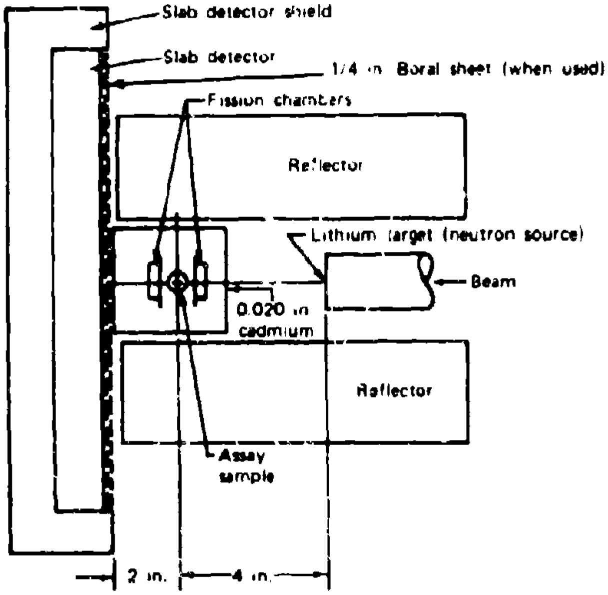

Figure 6.15 Schematic for a small sample delayed neutron assay system using a Van de Graaff generator.

cycle consists of irradiation for 35 ms, delay for 15 ms, counting for 40 ms, and delay for 10 ms. Total assay time for 300 cycles requires 30 s.

A large, shielded, temperature-controlled (±5°C) room is needed to contain the instrument. Cooling water for the target is required.

Major costs are as follows:

Accelerator	$250,000
Shielding	100,000
Electronics, detectors, and miscellaneous	50,000
	$400,000

Major Sources of Error

The discussion of errors for assays with 14-MeV generators (Section 6.2.1) applies to Van de Graaff accelerators as well. Additional errors may result from the neutron-producing reactions. Both neutron flux and energy are functions of the angle of emission of the neutron from the target. Though this is also true for the T(*d*,*n*) reaction used in 14-MeV generators, it is more pronounced for some other reactions. The net result is that, except for small volume samples, the interrogating flux and energies will vary significantly over the sample. Sample rotation will help minimize these effects as will the use of physical standards that closely approximate the sample in composition and size.

Measurement Control Requirements

System calibration requires the use of standards that closely resemble the samples being assayed. Some discussion of this topic appears in Section 6.1.2. The standards used should be prepared from well characterized material or should be assayed by an accurate method. The standards are typically measured at the beginning of a run for calibration purposes and at the end of the run to check for drift.

Data Analysis Requirements

The greatest calculational effort is that required to obtain the calibration function. Once this step is accomplished, determination of the material content for an unknown is simple. More effort is required in the two-spectra method to determine isotopic concentrations; i.e., two equations must be solved for two unknowns.

6.2.3 Isotopic Source Step Irradiation

Description of Method

An isotopic neutron source is used for interrogation radiation in some systems when signature radiation consists of delayed neutrons. Because neutron emission from these sources cannot be turned off, it is necessary, in order to avoid interference between signature and interrogation radiations, to separate the source and sample following irradiation by moving either the source or the sample. Source or sample transit times need to be of the order of 1 s so that most of the delayed neutron signal is not lost. Therefore, any sample movement is restricted to small samples.

Scope of Applications

This method has been used to assay Pu and fissile or fertile U in samples ranging from pellets to 55-gal. drums of waste and scrap. With proper detector shielding, highly radioactive samples (i.e., those containing fission products) can be assayed.

Summary of Performance

The performance of this method is summarized in Table 6.6.

Table 6.6 Summary of performance for isotopic source step irradiation with delayed neutrons[a]

Sample	Random Error (%)	Systematic Error (%)	Accuracy (%)
HTGR fuel rods	0.3	—	—
Light water breeder reactor (LWBR) pellets	0.1	—	1.5
U-Pu ingots; up to 4 kg each	—	—	3
LEU and HEU inventory samples; 5 to 500 mg ^{235}U per sample	—	—	2.9
Light water reactor (LWR) spent-fuel assemblies	5[b]	5[b]	—
HEU intermixed with furnace parts and reduction residues in 30-gal. drums	—	—	20
Waste contaminated with fission products in 55-gal. drums	—	—	40[b]

[a] Data entirely from literature survey.

[b] Estimated.

Equipment

Figure 6.16 is a schematic of the Shuffler assay system in which the isotopic source is moved (Ref. 22). It contains all essential system elements described in Section 6.1.4. The source transfer mechanism must be capable not only of rapidly moving the source away from the sample following irradiation but also of accurately positioning the source at the irradiation position. Two different methods for moving the source have been a[illegible] mechanical and pneumatic. The mechanical system gives more accurate positioning, but the pneumatic is faster and more flexible.

All systems described in this section use ^{252}Cf interrogation sources. These sources emit neutrons and gamma rays as a result of spontaneous fission of ^{252}Cf. The multiplicities and spectra of these radiations are comparable to those from induced fissioning of an SNM. (See Section 6.1.1.) Other isotopic sources could be used.

The measurement cycle consists of source retrieval for irradiation, sample irradiation, source removal, and delayed neutron (or gamma-ray) counting. Irradiation intervals may be as short as 1 s so that automated operation, including data recording, is required.

Step irradiation systems employing isotopic sources have been used to assay samples varying in size from a few milliliters to 55-gal. of waste. The cost of these systems will vary with system complexity, range of applications, and type and strength of the neutron source. The estimated cost of Shufflers is between $150,000 and $300,000. The cost of a delayed neutron pellet scanner is considerably higher.

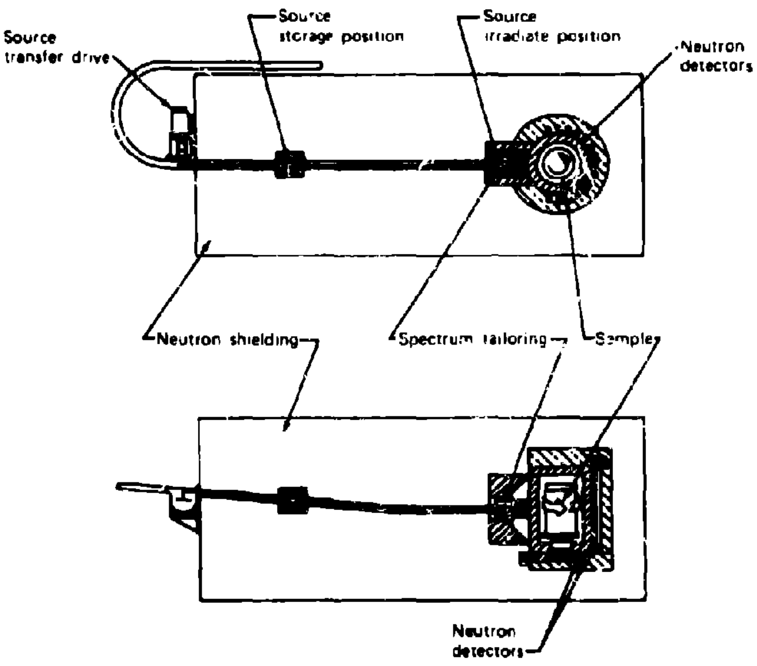

Figure 6.16 Schematic of a Shuffler assay system.

Major Source of Errors

Most errors that affect delayed neutron techniques employing accelerators (discussed in Section 6.2) will also affect the isotopic source step irradiation technique. Because different interrogation energies are being used, the relative importance of some of the errors may be different. One difference is that errors associated with accelerator instabilities are replaced by those associated with positioning and timing of the shuffled source or sample. In a well-made system, however, positioning errors should be small.

Measurement Control Requirements

System calibration requires the use of standards that closely resemble the samples being assayed. This subject was discussed in Sections 6.1.2 and 6.1.3.

Data Analysis Requirements

There are no unusual data analysis requirements. Data reduction involves, at most, a few simple algebraic manipulations. Automatic data recording plus a programmable calculator or minicomputer can make the entire operation automatic.

Survey of Selected Literature

Assay of U and Pu with a ^{252}Cf Shuffler (Refs. 22 through 24)

Various models of the Shuffler have been built to accommodate different sample sizes up to 55-gal. drums. For one model, the samples (U-Pu ingots, waste, and scrap) were packaged in cans 7 in. in diameter by 12 in. high. Another model was built to assay 30-gal. drums containing waste. Still another was designed for small samples, such as HTGR fuel sticks and inventory verification samples.

Figure 6.16 shows the main components of a Shuffler assay system. The source transfer is mechanical, using a Teleflex cable driven by a stepping motor. The sample is rotated to reduce the effects of radial inhomogeneities. Spectrum tailoring is used to reduce the relative response of fertile isotopes of U to less than 2% of that for ^{235}U while at the same time maintaining reasonable penetrability. Spectrum tailoring also modifies the axial flux to help compensate for the effects of different sample heights. The entire Shuffler is shielded for personnel protection.

A typical procedure for a measurement is as follows: The can is placed in the sampling area where a background count is taken with the source in the "away" position. Measurement cycles are then begun. The number of cycles depends partly on obtaining sufficient counts for the desired counting statistics. Typical measurement times are 200 to 500 s. For a tall sample with a significant axial flux nonuniformity, more than one measurement position may be needed.

The performance of the Shuffler varies, depending on the size of the sample and how well it is characterized. For HTGR fuel rods (Ref. 25) the precision was 0.5%. For larger, but still homogeneous, samples like U-Pu ingots up to 4 kg, calculations (Ref. 26) showed an expected error of 3%. Measurement of waste in 30-gal. drums showed an error of 20%, determined from a rough estimate of the contents of the cans (Ref.27).

Assay of Hot Waste in 55- and 80-gal. Drums (Refs. 28 and 29)

This potential application was for the assay of U and Pu waste in drums containing fission products with radiation levels up to 1000 R/h. Two different systems were proposed. The principal difference between these and the Shuffler described in the previous application is the addition of heavy shielding for the high gamma-radiation levels associated with hot waste.

One design (Ref. 28) is an above-ground installation as shown in Figure 6.17. Note the thick lead shield between the sample cavity and the

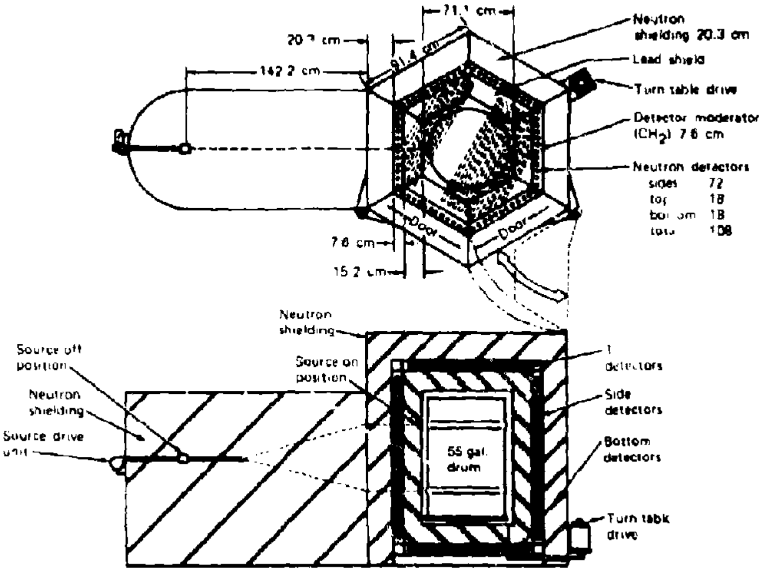

Figure 6.17 Artist's concept of an in-plant above-ground installation for isotopic source step irradiation. Two interrogation source positions and detectors located on top and bottom are used to improve the response uniformity.

detector. This shield reduces the gamma-ray background at the detector and provides the additional personnel shielding needed. The detector moderator was changed from cylindrical to hexagonal because calculations showed that there would be a flatter response with this configuration. Uniform axial irradiation is accomplished by using two source positions and alternately irradiating the drum from these two positions.

The other design (Ref. 29) is for a below-ground system in which most of the shielding is provided by the ground. This system was designed for 55- to 80-gal. drums. To improve the uniformity of axial response, the ^{252}Cf can be positioned at three locations along the side the drum. The below-ground system, equipped with a 1-mg ^{252}Cf source (2.3 × 10^9 n/s), is expected to have a detection limit of 1 to 2 g of SNM and an accuracy of 40%(1σ) for the assay of heterogeneous 55-gal. drums. The performance of the above-ground system is expected to be similar to that for the below-ground system.

Assay of LWBR Pellets With Neutron Pellet Assay Gauge (Refs. 30 and 31)

This application is for the assay of $^{233}UO_2$-ThO_2 pellets used in LWBR fuel rods; pellet sizes are 0.5 in. in diameter and from 0.5 to 1 in. in length.

Figure 6.18 is a drawing of the gauge. The irradiation and counting take place in a 5000-gal. water-filled tank used for shielding. Two sources, each containing 5 mg of ^{252}Cf, are in the middle of the tank. The sample is loaded into the sample holder in the glove box, transported to the ^{252}Cf sources, and irradiated for 100 s. It is then moved to the detector station consisting of six ^3He counters in a moderator and counted for 100 s. If desired, a background count is taken before the assay sequence is started. Total assay time is about 5 min.

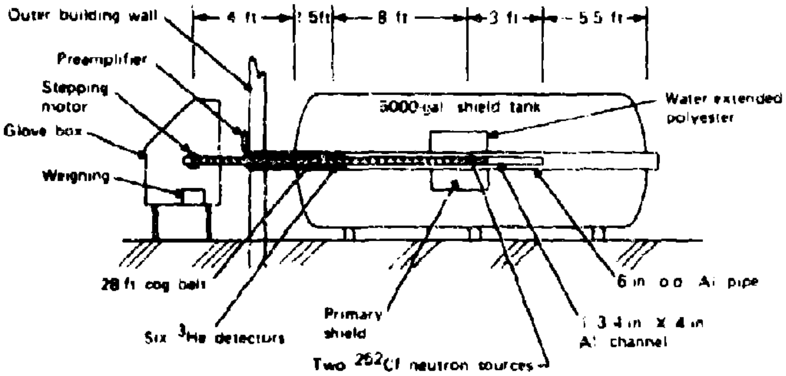

Figure 6.18 Sketch of LWBR pellet assay gauge.

The measured precision was 0.1% RSD, slightly greater than expected from counting statistics. The gauge showed small sensitivities to fuel pellet length and diameter. Comparisons with chemical assay showed a 1.5% difference (Ref. 31).

6.2.4 Nuclear Reactor

Description of Method

A nuclear neutron reactor has been used as an interrogation source with delayed neutrons as the signature radiation (Refs. 11 and 32 through 35). A transfer system is used to move the sample from the reactor to the detector for counting. This technique can be considered as an alternative and sometimes as a replacement to high-accuracy wet chemical, X-ray fluorescence, and other analytical methods.

Scope of Applications

An assay system using delayed neutrons from reactor irradiation is applicable to the determination of microgram to gram quantities of fissile materials in small samples. Fertile materials can also be determined by a proper suppression of the reactor thermal neutron flux during irradiation.

Only limited use has been made of reactors in active NDA. One use was to determine ^{235}U and ^{232}Th in HTGR fuel sticks. This application covered both liquid and solid samples. The liquid samples were made from highly enriched uranium ox[illegible] and were sometimes mixed with thorium oxide with ratios of Th/U from 4 to 20 to simulate fuel sticks. Other liquid samples were made from crushed, burned, and dissolved fuel sticks. Measurements were made directly on sticks (1.4-cm diameter by 5-cm long). All samples were encapsulated in heat-sealed polyethylene cylinders.

Summary of Performance

Numerous intercomparisons with chemical assay show that the root-mean-square (RMS) deviation between this technique and wet chemistry for ^{235}U assay in HTGR fuel sticks is + 0.5% (relative). This can be construed as a conservative estimate of the systematic error for a specific application. Calculations suggest that ^{232}Th in the HTGR fuel sticks could be assayed with an accuracy of approximately 1%.

Repeatability was determined over a period of years by comparing standard samples to a flux monitor (a sample measured immediately after a standard or unknown sample and used to correct for any changes in the neurtron flux). The random error for 30 measurements was between 0.2% and 0.3% RSD. The RMS deviation in the yearly averages over a period of 3 yr was 0.27%. Thus a fair estimate of random errors, including system stability, is about 0.3% RSD.

Equipment

The basic components of a reactor-based delayed-neutron system are a nuclear reactor, a pneumatic sample transfer system, and a highly efficient thermal neutron detector. Because a 30-s delay is used between irradiation and counting, the timing requirement placed on the transfer system is not stringent. The design requirements for the delayed neutron detector are straightforward: high efficiency, flat response over the sample size, and lead shielding to provide personnel protection. The detector is located to minimize the neutron background from the operating reactor. The sensitivity of this method can be very high, for example, about 4×10^4 counts/μg of ^{235}U. Hence, one has to select the power of the reactor (or sample size) so it is commensurate with a maximum allowable initial counting rate of about 10^5 count/s. The measurement time is such that a throughput of 30 samples/h is readily achieved.

If fertile materials are to be assayed, the in-core pneumatic system receiver will need to be shielded with thermal neutron absorbers such as ^{10}B and Cd.

Major Sources of Error

A general discussion of errors appears in Section 6.1.3. In one use, the assay of ^{235}U in fuel sticks, self-attenuation proved to be a problem.

Measurement Control Requirements

As with other active NDA techniques, standards representative of the samples are required. See Sections 6.1.2 and 6.1.3 for general discussions of standards.

Data Analysis Requirements

The data reduction can be done manually in real time because the computations are simple and the time between samples, approximately 2 min, is adequate but a large throughput would make computer calculations desirable.

6.3 SUBTHRESHOLD NEUTRON SOURCE TECHNIQUES

The need to design active NDA systems so that interrogation radiation does not interfere with signature radiation has led to the use of "subthreshold neutrons" for interrogation. Subthreshold neutrons are neutrons with energies less than the approximately 0.5 to 1.0-MeV fission thresholds for fertile isotopes. By comparison, the median energy for prompt fission neutrons is approximately 1.6 MeV. If interrogation radiation consists of subthreshold neutrons and a detection system is used that discriminates against these neutrons, then prompt neutrons can be counted in the presence of interrogation radiation. Another advantage of using subthreshold neutrons for interrogation is that there will be little or no interference with the assay of fissile isotopes by fertile isotopes. Because of this, subthreshold neutrons are particularly effective when low-enrichment fuel is assayed. If the interrogation neutron energies are in the keV range, they will penetrate samples of small to intermediate size, and sample attenuation should not be a problem. Subthreshold sources used by systems to be described are ^{124}Sb-Be and ^{226}Ra-Be (γ, n) sources and spectrum-tailored ^{252}Cf sources. If a Van de Graaff accelerator is available, (p,n) reactions can be used to produce low-energy neutrons.

Photoneutron sources are those employing the (γ,n) reaction. Beryllium-9 has the lowest photoneutron threshold of any naturally occurring isotope, 1.67 MeV, and is commonly used as a target for photoneutron sources. Deuterium has the next lowest threshold, 2.23 MeV, and has also been used as a target material in photoneutron sources. Reactor-produced ^{124}Sb is a common gamma material in photoneutron sources. The neutron spectrum for a ^{124}Sb-Be source consists essentially of a discrete neutron energy of 24 ± 2 keV. The half-life of ^{124}Sb is only 60 days, and this is a distinct disadvantage. An isotope that overcomes this disadvantage is ^{226}Ra with a half-life of 1600 yr. Radium-226 is expensive, though, and has a complex gamma-ray spectrum that contains a high-energy component that, in a Ra-Be(γ,n) source, yields neutrons with energies above the fertile threshold. About three-quarters of all neutrons are produced with energies of 55 or 87 keV, and the rest with energies up to 700 keV. Because gamma rays can easily penetrate the walls of a container, the Be target material and the gamma-ray emitter can be packaged separately. Then, when the neutrons are desired the gamma-ray emitter container and the target container are placed into juxtaposition. This ability to turn the neutron emission on and off is a distinct advantage of (γ,n) sources over (α,n) sources.

Some neutron detectors have an effective threshold of approximately 0.5 MeV and are therefore insensitive to subthreshold neutrons. These include solid and liquid scintillators that have the highest efficiency for fission neutrons among all fast neutron detectors. The main deficiency of these detectors is a high sensitivity to gamma rays. Some discrimination against gamma rays can be obtained by employing a pulse-shape discrimination circuit that uses the difference in scintillation decay times between gamma rays and neutrons. A detector that is relatively insensitive to gamma rays is the gas-filled proportional counter. Those filled with ^{4}He, hydrogen, or methane depend on neutron scattering to produce the electrical signal. A ^{4}He detector has an effective threshold for neutron detection of approximately 0.5 MeV, while hydrogen and methane detectors are useful for counting neutrons with energies from 10 keV to a few MeV. These detectors can operate in gamma-ray fields up to approximately 100 mR/h. Fast neutron detectors that can operate in high gamma-ray fields are fission chambers with a fertile isotope such as ^{238}U, ^{232}Th, or ^{237}Np as the neutron converter. A disadvantage of fission chambers is very low detection efficiencies. A more detailed discussion of detectors and their suitability for use under various conditions can be found in Reference 36

6.3.1 Isotopic Photoneutron Sources

Description of Method

This method uses subthreshold neutrons from an Sb-Be or Ra-Be (γ,n) isotopic source for interrogation radiation and prompt neutrons for signature radiation. There is a strong gamma-ray background associated with (γ,n) sources, and equipment design requires substantial amounts of Pb to shield the fast neutron detectors.

Scope of Applications

Subthreshold neutron source techniques are particularly well suited for assaying fissile isotopes in low enrichment fuel and fuel assemblies. The technique has also been applied to waste and scrap in containers up to 5 gal.

Summary of Performance

Although a number of devices have been built, very little performance data have been collected. The devices were generally built to test the feasibility of the idea and to see what the major contributions to the error might be. The accuracies obtainable with this technique range from 1% to 5%. Results are summarized in Table 6.7.

Table 6.7 Summary of performance for isotopic photoneutron source assay[a]

Sample	Assay Time (s)	Random Error (%)	Systematic Error (%)
HTGR fuel sticks	2000	1	2
UO_2 loose powder, 9.3 g^{2}	1000	1.8	<1[b]
Waste and scrap in 1 to 5-gal cans, 10 g to 1 kg U per sample	—	2 to 10[b]	1 to 3
^{235}U-^{239}Pu fuel pins	300	^{235}U: 1[b] ^{239}Pu: 2[b] ^{240}Pu: 2.5[b]	— — —
Rover fuel rods (7 rods measured together)	150	0.85	0.4

[a] No data in this table are from the users' survey of production facilities.

[b] Estimated.

Equipment

The design of an assay instrument using an Sb-Be or Ra-Be source is very flexible because the source can be made in a number of geometries such as spherical, annular, or cylindrical. The neutron intensity is determined by the strength of the gamma-ray source and the thickness of Be.

The Be also acts as a neutron moderator. A Pb gamma-ray shield usually surrounds the source. The sample to be measured and the detector are located in the shielding. The position of the sample can be varied depending on the source neutron strength, desired signature radiation intensity (i.e., sensitivity), and the acceptable level of gamma-radiation background. The detection system should respond only to fast neutrons and be insensitive to or shielded from the high gamma-ray background. Threshold fission chambers, ^{4}He proportional counters, and liquid scintillation counters with pulse shape discrimination can be employed depending on the level of the gamma-radiation field. Figure 6.19 is a diagram of an Sb-Be assay system.

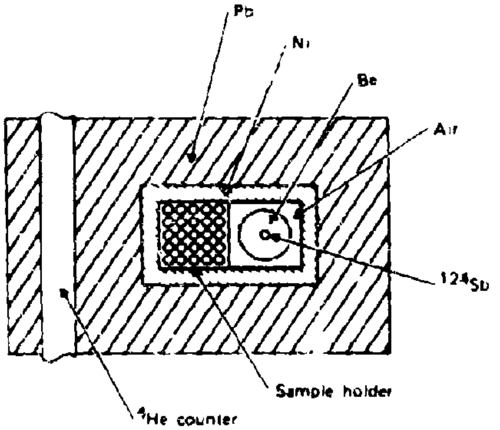

Figure 6.19 Experimental photoneutron assay system (top view).

Major Sources of Error

A specific source of error for a system employing a (γ,n) interrogation source can be the gamma-ray background from the source. Thick Pb shielding and discrimination against gamma rays by the detector can reduce this background to an acceptable level. Highly radioactive samples in close proximity to the Be mantle of the source can produce photoneutrons in the Be, varying the interrogation source intensity slightly. Other potential sources of error include those mentioned in Section 5.1.3.

Measurement Control Requirements

Because all active NDA techniques are relative measurements, standards that resemble samples as closely as possible are required. See Sections 6.1.2 and 6.1.3 for discussions of this matter.

Data Analysis Requirements

Data analysis is straightforward and can be done with a small calculator.

Survey of Selected Literature

Assay of Small ^{235}U Samples Using Sb-Be Neutrons (Ref. 37)

This assay system, diagramed in Figure 6.19, was designed for small samples containing up to a few tens of grams of ^{235}U. The sample holder is a 10 cm square array with 25 sample positions. The system response in the central nine positions is flat, but there is up to a 15% deviation in the outer sample positions. The Pb serves a dual purpose, as a gamma-ray shield for the detector and as a neutron reflector. System cost is estimated to be approximately $75,000.

Figure 6.20 shows the response of this system to small amounts of ^{235}U. When a 2-Ci ^{124}Sb source was used, the random error for a 1000-s measurement of 9.3 g of ^{235}U (loose UO$_2$ powder) was 1.8%. The system sensitivity can be increased, by using multiple detectors, to a rate of 2 counts/s·g·Ci. Thus a 100-g ^{235}U sample could be measured to a statistical precision of 0.5% in 20 s when a 10-Ci ^{124}Sb source is used. The systematic errors for small samples of pure material or clean scrap containing up to about 50 g are estimated to be <1%.

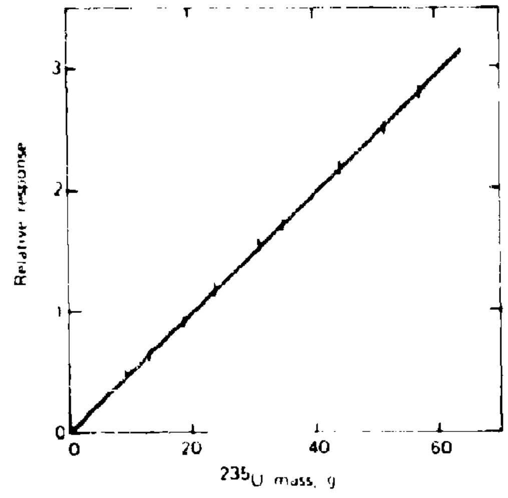

Figure 6.20 Photoneutron assay system response as a function of ^{235}U mass with samples placed in the nine central sample positions.

Photoneutron Assay of HTGR Fuel Sticks (Refs. 38 and 39)

HTGR fuels sticks, 2-in. long and 1/2-in. diameter, consisting of highly enriched ^{235}U and Th, were assayed in this application.

A device was built to test the feasibility of using an Sb-Be source as part of an assay instrument. It consists of a Pb block with channels to accommodate the source, sample, and detector. The source, Be cylinders with a central hole for an ^{124}Sb line source, is located in the center of the block. There is about 8 in. of Pb between the source and the slots for the fuel and detector, a proton recoil liquid scintillator. Pulse shape discrimination is used to reduce further the response to gamma rays. Assay times are a few minutes. The cost of this system is estimated to be approximately $40,000.

Tests showed that self-shielding is present when ^{235}U plates 0.06-in. thick are assayed, for at this thickness the count rate per gram is 7% less than it is for plates 0.03-in. thick. A nonlinear calibration curve is therefore required.

Table 6.8 shows data from different methods for measuring HTGR fuel sticks. Comparison of the active NDA values with the manufacturer's values and with the results of passive measurements made using 186-keV gamma rays from ^{235}U, indicates an accuracy of about 2% (the random errors were about 1%). This method is limited to samples that do not have a high gamma-ray intensity.

Table 6.8 NDA of ^{235}U in HTGR fuel elements

Manufacturer's Values (g)	Active NDA Results (g)	Passive NDA Results (g)
0.94	0.97 ± 0.01	0.94 ± 0.005
0.84	0.84[a]	0.84[a]
0.74	0.74 ± 0.02	0.74 ± 0.005

[a] This sample served as a standard for both active and passive NDA.

Photoneutron Assay of FFTF Fuel Rods (Refs. 40 through 42)

This photoneutron assay device is designed to assay FFTF fuel rods. The rods are 93-in. long with 30 to 39 g of Pu mixed uniformly in natural or depleted U loaded in the central 36 in. of the rod. This design, like that for the previous system, shows the flexibility in geometry that an Sb-Be source allows. In this case, the source is an annulus about 7 cm in outside diameter and 1 m long. The center is the sample volume. Surrounding the source is a Ni reflector that increases the flux in the central region by a factor of two. Around the Ni is a Pb gamma-ray shield, then the detectors, followed by an Fe reflector to increase the detector counting rate. The detector used is the ^{4}He recoil type, chosen because of its relatively low sensitivity to gamma rays. Fifteen of these detectors were used, all connected to a single preamplifier. The average energy of the interrogating neutrons is about 0.1 keV, and the ^{4}He detectors are insensitive to source neutrons of this energy. No results are available.

EURATOM Photoneutron Assay for Bulk Samples (Ref. 43)

The material type is not specified, but it probably is waste and scrap from fuel production. The source for this system consists of a cylinder containing Sb surrounded by a Be cylinder. The Be can be positioned pneumatically so the source can be turned on and off. This allows (theoretically at least) one to measure delayed as well as prompt neutrons. A 3-Ci source is placed in a 55-cm diameter, 60-cm high, Pb cylinder adjacent to a 40- by 60- by 60-cm cavity. At the opposite side of the cavity from the source is the detector, a bank of 18 ^{4}He recoil counters. The neutron spectrum can be varied grossly by inserting either a moderator slab to thermalize the neutrons or a B_4C plate to harden the spectrum. The sample is rotated during measurement, and it can be scanned vertically. Response curves for clean U (93% ^{235}U) bearing materials for this system are shown in Figure 6.21. The systematic errors inferred from this figure for the materials studied are probably a few percent.

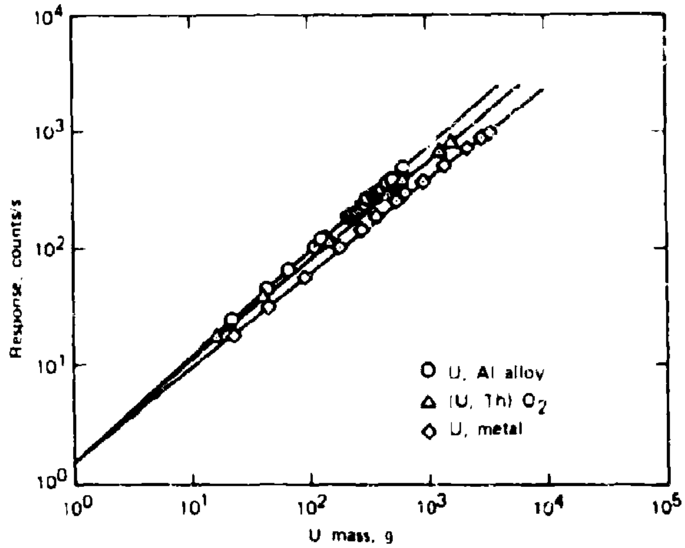

Figure 6.21 Calibration curves for a EURATOM Sb-Be assay system.

EURATOM Photoneutron Assay System for Fuel Pins (Ref. 44)

The $(U,Pu)O_2$ fuel pins assayed are 48.5 cm long and 6.7 mm in diameter. The composition is 45% ^{235}U and 22% ^{239}Pu (relative to total U plus Pu). The device (see Figure 6.22) is built around two pneumatic systems, one for moving the Be mantle to switch the source on and off,

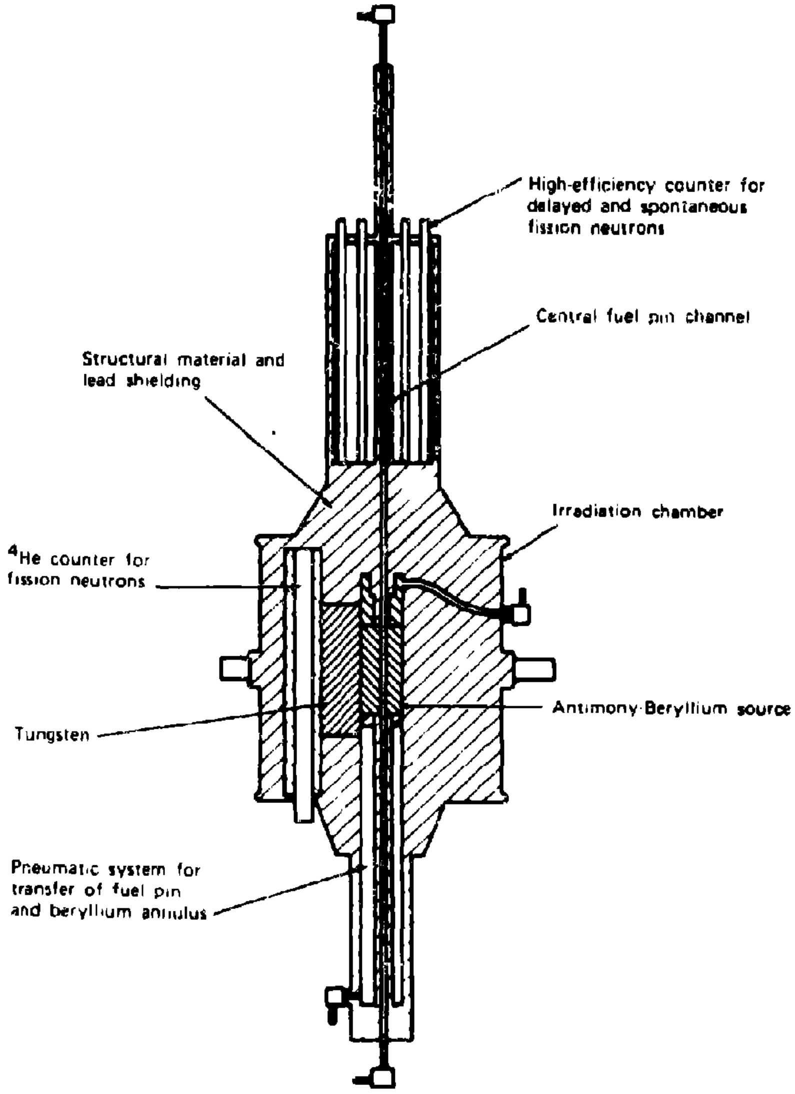

Figure 6.22 EURATOM Sb-Be system for measuring stimulated and spontaneous fission in U-Pu fuel pins.

and the second for moving the fuel pin from the irradiation position to a counting position to count delayed neutrons. The source consists of an inner annulus of Sb and an outer annulus of Be. The central region accommodates the fuel pin. One ^{4}He recoil detector is used to detect prompt fission neutrons. The delayed neutron detector is a ring of four ^{3}He counters surrounding the pneumatic tube above the irradiation chamber. The ^{3}He detectors can also be used to passively measure spontaneous fission neutrons to determine ^{240}Pu content. The assay time is about 5 min. No results were reported; however, calculations indicate random errors of 1% for ^{235}U, 2% for ^{239}Pu, and 3% for ^{240}Pu.

Assay of Irradiated Rover Fuel Using a Ra-Be (γ,n) Source (Ref. 45).

Irradiated fuel rods consisting of 93% enriched ^{235}U in a graphite matrix and having a radiation level of 15 R/h at contact were assayed. This device was built for the Rover (nuclear rocket propulsion) program. A ^{226}Ra-Be (γ,n) source is used to produce photoneutrons. Two Ra sources, with activities of 2.0 and 2.5 Ci, are positioned above and below the sample cavity. (See Figure 6.23.) Surrounding this is a Pb and Ni neutron reflector. Additional Pb shielding is placed around the detectors to protect them from the gamma-ray activity of the source and sample. The detectors, 12 ^{4}He proportional counters, detect the prompt fast fission neutrons created in the sample. Rejection of all source neutrons is achieved by pulse-height discrimination. The sample is scanned by being pushed through the sample cavity with a pushrod and stepping motor assembly. Assay time for a single tube (seven fuel rods) is 150 s. For a single measurement, the total accuracy is 1% (0.85% statistical uncertainty and 0.4% systematic uncertainty due to the standards used). Measurements of 5400 rods showed a deviation of 0.6% from the book value.

6.3.2 Fermi Age Technique

Description of Method

In Section 6.3.1 a system was described in which interrogating neutrons from an Sb-Be source were discriminated against when signature (fission) neutrons were counted by using detectors with a detection threshold of approximately 0.5 MeV. Another way of counting fission neutrons in the presence of Sb-Be neutrons is to use differences in their mean free paths (i.e., the mean distance traveled between interactions). In water a 24-keV neutron has a mean free path of 0.54 cm, and a 2-MeV neutron has one of 2.8 cm. Thus, when signature neutrons are moderated to thermal energies in water, they will diffuse more than will interrogration neutrons. If equal numbers of interrogation and signature neutrons

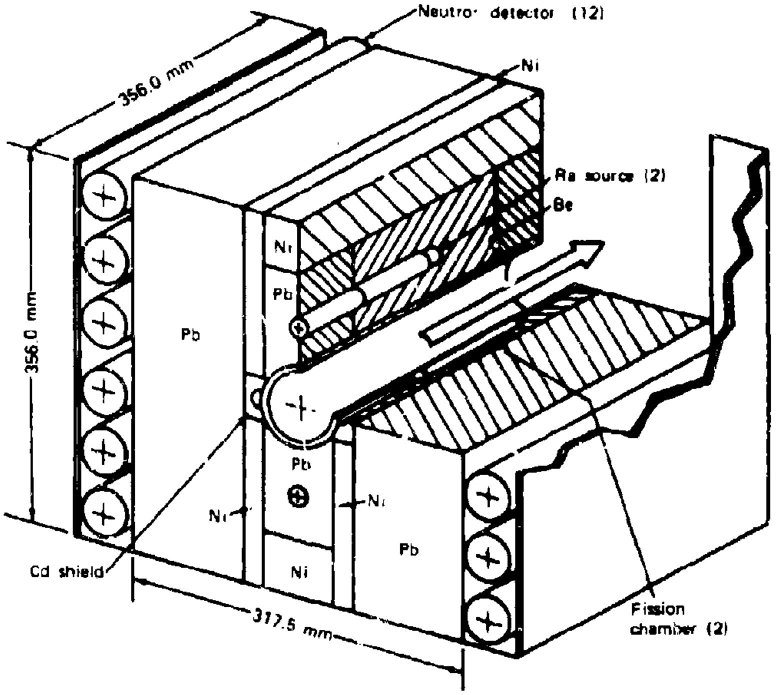

Figure 6.23 Irradiation region of the Ra-Be(γ,n) assay system for measuring ^{235}U content in irradiated Rover fuel rods.

are emitted at some point in water, then at a given distance from this point, 12 cm for instance, the ratio of thermalized interrogation neutrons to thermalized signature neutrons will be much less than one. Because both signature and interrogation neutrons will be counted when a sample is being assayed, the background interrogation counting rate must be subtracted. The closest sample-to-source separation at which the measurement can be done is determined by the signal-to-background ratio. (The name "Fermi age" comes from a mathematical model describing the loss of energy by neutrons in nonabsorbing or weakly absorbing media.)

Scope of Applications

This technique is applicable to determining the fissile content of small- and medium-sized samples such as fuel elements, fuel rods, and waste and scrap in 5-gal. containers. It is also applicable to measuring irradiated fuel contaminated with fission products.

Summary of Performance

Only two devices using the Fermi age technique have been built and only one measurement was done with standards. One device (Ref. 46) gave an accuracy of 10% with an assay time of 100 s. Calculations and an improved experimental technique, however, seem to indicate that accuracies of 1% are possible when 1 g of U is measured. The estimated precision for the other device (Ref. 47) is 1% with a 1-min assay time.

Equipment

An experimental arrangement for using the Fermi age technique to assay irradiated and unirradiated HTR fuel (composed of uranium, thorium, and graphite) is shown in Figure 6.24. The photoneutron source consists of an annulus of Be with two slots to hold ^{124}Sb capsules. The detector is a BF_3 counter in a pure water moderator. Between the detector assembly and source sample assembly is a borated water moderator. The

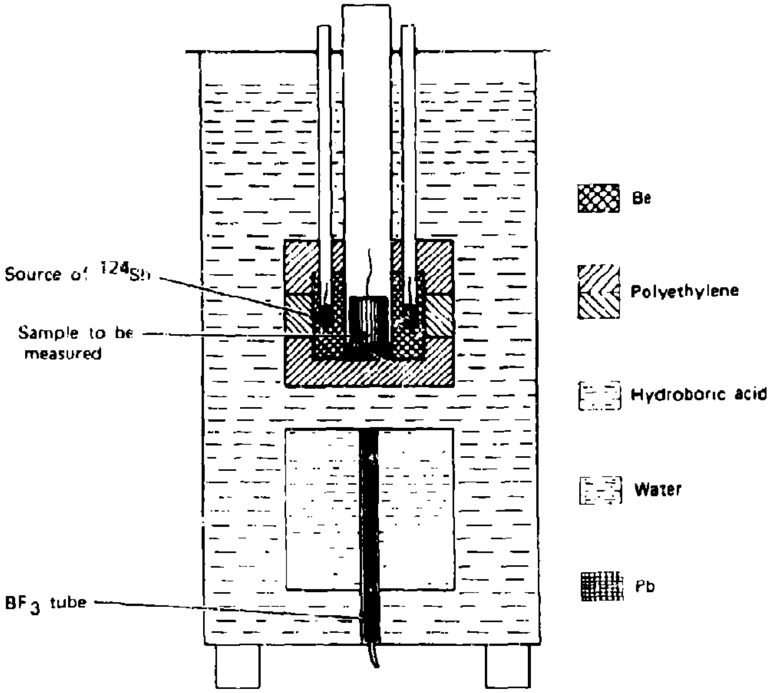

Figure 6.24 An experimental arrangement for the Fermi age technique.

boron will absorb thermalized neutrons and, because of the difference in mean free paths between interrogation and signature neutrons, the former will preferentially be absorbed. A Pb gamma-ray absorber is located between the sample and the detector. Assay time is dependent on the source strength and desired counting accuracy. Typical assay times are of the order of 100 s.

Another system was built to assay LWR fuel rods 0.88 cm in diameter and 1 m long. In this system the source is a Be cylinder with a central hole for the fuel rod. Close to the rod are channels for the Sb. The source-sample assembly is mounted in the center of a tank of water. A 1-m long ^{3}He detector, mounted parallel to the fuel rod, is used. Cost estimates for systems based on the Fermi age technique are between $100,000 and $150,000.

Major Sources of Error

A major source of error is moderation of the interrogation source spectrum by matrix materials. This will increase the fission rate because of the higher fission cross sections at lower energies. Hydrogenous matrix materials can be particularly troublesome. In these tests it was found that the addition of 50% water by volume increased the count rate 15%. This was the result of spectrum softening and, therefore, increased fissioning in the sample. Some compensation for this effect is possible, though, by additional measurements with a ^{235}U fission detector as a flux monitor. Another problem specific to the use of photoneutron source occurs when samples with high gamma-ray energies and intensities are measured. Gamma rays having energies greater than 1.67 MeV interact with the Be mantel of the Sb-Be source to produce neutrons. This effect can be estimated by measuring the response with the Sb portion of the sources removed and the Be mantel and sample left in place.

Measurement Control Requirements

Tests (Ref. 46) made with one system indicated the need for good standards. General discussion of measurement control and sources of error are found in Sections 6.1.2 and 6.1.3.

Data Analysis Requirements

There are no special requirements for data analysis.

6.3.3 Moderated ^{252}Cf

Description of Method

A disadvantage of using Sb-Be sources in active NDA is their short half-lives and high gamma-radiation levels. Other subthreshold sources such as ^{241}Am-Li(α,n) have limited neutron yield. In some applications these disadvantages can be circumvented by using intense, small volume, ^{252}Cf neutron sources. To use ^{252}Cf to assay fissile isotopes in the presence of fertile isotopes, however, the interrogation energy spectrum must be softened. With proper tailoring, the interrogation spectrum can be made largely subthreshold but still harder than that provided by photoneutron sources. A harder spectrum means greater sample penetrability, and larger samples can be measured before attenuation becomes severe. Interrogation radiation is discriminated against by using threshold detectors such as ^{4}He proportional counters or fission chambers. Prompt neutrons are used as the signature radiation.

Scope of Application

This technique has been applied to the assay of LWR fuel rods and HTGR fuel sticks. It was also studied for the measurement of the residual fissile content of spent fuel assemblies. The method, in general, can be applied to small- to medium-size amounts of SNM in solids, such as process material, and in scrap and waste in 1- to 55-gal. containers. Accuracies would range from 1% to 50% depending mostly on the material homogeneity, the matrix type, and the container size.

Summary of Performance

The performance of this technique is summarized in Table 6.9.

Table 6.9 Summary of performance for the subthreshold technique employing a moderated ^{252}Cf source[a]

Sample	Assay Time (min)	Random Error (%)	Systematic Error (%)	Accuracy (%)
HTGR fuel sticks with ≈1 g ^{235}U and 7 g ^{232}Th	10	0.6	$\ll 1^{b}$	−0.77 to −1.55 (bias)
Pressurized water reactor (PWR) fuel rod with UO_2 or UO_2-PuO_2 pellets and boiling water reactor (BWR) fuel rods	1	—	—	1 to 1.5
Spent LWR fuel assemblies	≈120	—	—	5^{b}

[a] No data in this table are from the users' survey of production facilities.
[b] Estimated.

Equipment

To illustrate the location of the components of fuel-rod scanners employing a moderated ^{252}Cf source, a cross-sectional view is shown in

Figure 6.25 (Ref. 48). The source, located at the center of a cylindrical tank, is surrounded, in this case, by a tungsten alloy, polyethylene, and heavy water. Other materials could make up the tailoring-moderating assembly. The sample is positioned near the periphery of the moderator to achieve a high fissile-to-fertile ratio. Detectors surround the sample cavity. Standard off-the-shelf electronics are used.

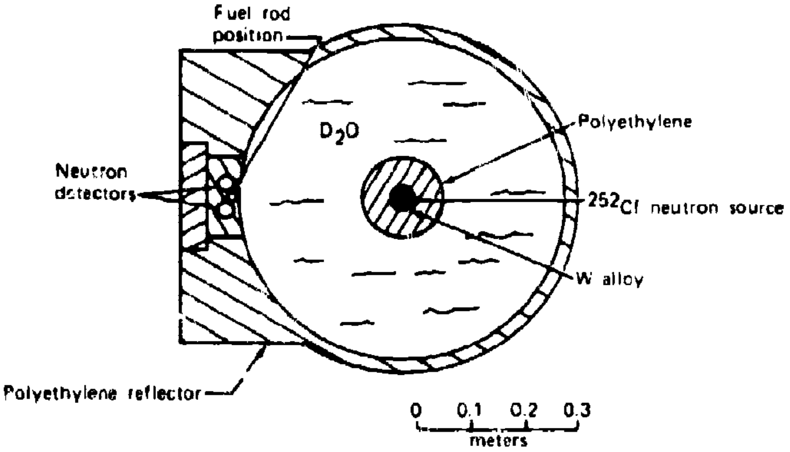

Figure 6.25 Cross-sectional view of the Oak Ridge fuel-rod scanner.

Major Sources of Error

The major sources of error are matrix effects (especially from hydrogenous material), fissioning of fertile isotopes, self-shielding in the sample, and flux nonuniformities over the sample volume. These can be minimized by having representative standards and a well-tailored source spectrum.

Measurement Control Requirements

Representative standards are a must, as with other active NDA techniques. The instrument should be calibrated at the beginning and end of a run, and periodic checks must be made for drift.

Data Analysis Requirements

There are no special data analysis requirements as calculations are straightforward.

Survey of Selected Literature

Oak Ridge Scanner (Ref. 48)

HTGR fuel sticks, 4.5 cm long, containing 1 g of ^{235}U and 7 g of ^{232}Th, have been assayed. Figure 6.25 is a drawing of the assay device. A 1-mg ^{252}Cf source is located in a tungsten and polyethylene thimble that is centered in a heavy water bath. The diameter of the cylindrically shaped heavy-water tank is 60 cm and the height is about equal to its diameter. Embedded in a polyethylene reflector at the side are the sample channel and two ^{4}He proportional counters biased to discriminate against lower energy moderated neutrons from the source.

Standard rods were repeatedly assayed over a 3-week period to determine the precision of the assay instrument. The relative standard deviation was 0.58%. The fuel rods were divided into three groups, and all rods in each group were assayed. Samples were then assayed chemically. Active NDA and chemical assay results were compared using a linear calibration curve. The differences between active NDA and chemical assay results were −0.77%, −0.88%, and −1.55% for the three groups with a relative standard deviation of 0.58%.

Total Fissile Fuel-Rod Scanner (Refs. 49 and 50)

Material assayed included PWR fuel rods with either UO_2 or UO_2-PuO_2 pellets and BWR fuel rods with an enrichment of 2.34%. This rod scanner measures only the total fissile content of a rod and not the pellet-to-pellet variations. A 100-μg ^{252}Cf source is moderated strongly using heavy water. Strong moderation is needed to reduce the background of unmoderated fast neutrons from the source. Even so, there is still a measurable background. This constant background is used as a signal to correct for long-term drifts. Measurement of the fission neutron signature radiation is made using energy-biased ^{4}He recoil detectors. Six fuel rods can be measured simultaneously. Data collection and reduction are performed with a programmable calculator. The cost of this system, excluding the cost of the heavy water, is approximately $200,000.

The main sources of error for this device are counting statistics, calibration curve uncertainties, and fuel length variations. The accuracy of the device for a single rod is 1% to 1.5% at the 1-σ level for fuel rods containing 30 to 120 g of ^{235}U. When 500 or more rods are assayed, the total ^{235}U content should be known to better than 0.25% at the 1-σ level.

Spent-Fuel Assembly Assay (Ref. 51)

A study was done to determine whether the subthreshold neutron source technique could be used for the assay of the total fissile content of spent fuel assemblies from LWRs having burnups up to 30,000

MWD/MTU. The outcome of the study is the proposed device shown in Figure 6.26. It is intended to be located and operated in the spent-fuel storage pool.

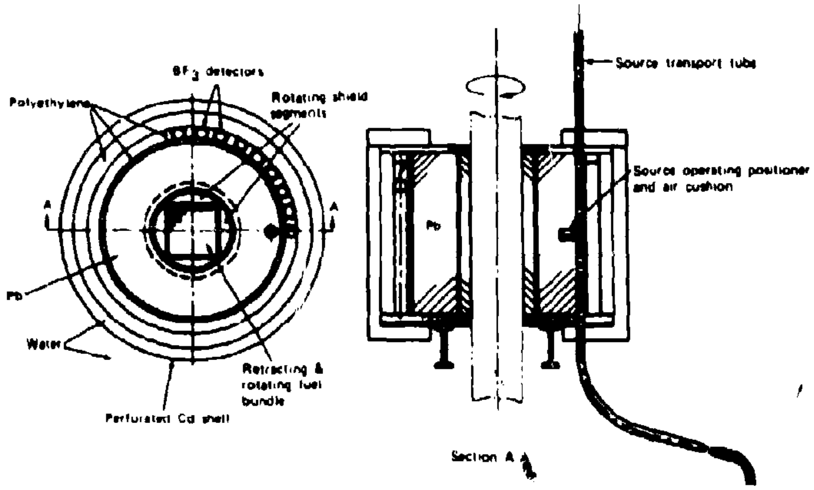

Figure 6.26 A proposed design for the assay of the residual fissile content in a spent-fuel assembly.

For a measurement, a spent-fuel assembly is placed at the center of the Pb annulus and rotated. Surrounding the Pb annulus is the detector assembly consisting of BF$_3$ or ^{3}He counters in a polyethylene moderator. The overall diameter is approximately 1 m. Total fissile content is measured using prompt fission neutrons for the signature radiation. Sources that could be used and their approximate strengths are ^{252}Cf (10 μg) and Sb-Be (4 Ci). The source is located in a pneumatic tube in the Pb annulus. It can be positioned along the length of the assembly to obtain some idea of the spatial distribution of fissile material. Assay times are on the order of a couple of hours. A method was also proposed for determining the ^{239}Pu/^{235}U ratio either by measuring the delayed neutron yield or by measuring the prompt neutron yield after the neutrons had passed through a gadolinium filter. A spent-fuel assay system will cost approximately $300,000.

The overall estimated uncertainty is 5%, provided corrections for neutron absorption by fission products, ^{238}U fast fission, and self-absorption can be made with an uncertainty of about 3%. Neutron self-absorption is the largest contributor to the systematic error.

6.4 COINCIDENCE TECHNIQUES

It is necessary in the design of any active NDA system to ensure that radiation from the interrogation source does not interfere with signature radiation. One way of accomplishing this is to use coincidence counting techniques.

The fission process results in the emission of several prompt neutrons and gamma rays. The average number of prompt neutrons depends on the fissioning isotope and varies from about two per fission at thermal energies to about five per fission at 14 MeV. There are also about seven prompt gamma rays per fission. If the interrogation source emits only one neutron or gamma ray at a time, then requiring the coincident detection of two or more neutrons or gamma rays or both[1] will be a way of discriminating against interrogation radiation. Even if more than one particle at a time is emitted by the interrogating source, it may be possible to shield the source or collimate the interrogation radiation to minimize this background.

Coincidence circuits are classified as either "fast" or "slow." The distinction between them is the time allowed for a coincidence to occur; i.e., after one particle is detected how much time is allowed for the detection of all remaining particles, each by a separate detector, for the coincidence requirement to be satisfied and a count to be registered. "Fast" systems are generally those for which 100 ns or less are allowed for the coincidence requirement to be satisfied. "Slow" systems typically have coincidence times ranging from 10 to 100 μs. With an active NDA fast coincidence system, scintillation detectors count gamma rays and unmoderated neutrons. With a slow system, BF_3 or ^3He detectors are used to count thermal neutrons. The relatively long coincidence times for slow systems are dictated by the long times neutrons remain as free particles in the moderator. A diagram of a two-detector coincidence circuit is shown in Figure 6.10.

Isotopic interrogation sources are used in active NDA coincidence systems. Such sources include ^{241}Am-Li(α,n), ^{238}Pu-Li(α,n), ^{241}Am-Be(α,n), and ^{252}Cf. The first two employ the reaction

$$^{7}Li + \alpha \rightarrow {}^{10}B + n \qquad (6-5)$$

with the alpha particles coming from radioactive decay of ^{241}Am or ^{238}Pu. Neutrons from these sources have a spread of energies from 0 to 1.5 MeV, with an average energy of approximtely 0.5 MeV. Many of these neutrons are subthreshold; they have energies below the fission thresholds for fertile isotopes, which is an advantage when assaying for fissile isotopes. The ^{241}Am gamma-ray energy spectrum includes a rather intense line at

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[1] Hereafter "particle" will be used in place of "neutron or gamma ray or both."

60 keV, but this is a relatively low energy that is easy to shield against. ^{241}Am-Be(α,n) sources use the reaction

$$^{9}\text{Be} + \alpha \rightarrow {}^{12}\text{C} + n \qquad (6\text{–}6)$$

and the neutron spectrum ranges from 0 to 11 MeV, with an average energy of approximately 4.3 MeV. A 4.43-MeV gamma ray is emitted in coincidence with approximately 70% of the neutrons.

Californium-252 sources, as described earlier, emit neutrons and gamma rays as a result of spontaneous fission. The multiplicities and spectra of these radiations are comparable to those resulting from fissioning of SNM. Because of this similarity, when ^{252}Cf is used as an interrogation source, it must be well collimated to reduce interference with signature radiation.

Coincident detection does not always signify coincident emissions. Source emissions occur randomly in time, but several could occur and be detected within the coincidence time and produce a count. These "accidental" counts are especially significant in slow coincidence systems in which they can constitute a large fraction of the total count. Accidental counts can be reduced by requiring the coincident detection of more than two particles. This improves the signal-to-background ratio (the ratio of counts from desired fission events to counts from accidental events), but it also reduces the signal intensity. Most systems with four detectors are often set to require the coincident detection by any three of the four detectors, 3/4. This is a compromise between 2/4, which has a better signal intensity than 3/4 but a poorer signal-to-background ratio, and 4/4, for which the reverse is true. Sometimes data are accumulated simultaneously for several types of coincidences such as 2/4, 3/4, and 4/4. The ratios of the different multiplications can be used to correct for various effects such as self-shielding, sample geometry, and nonuniform distribution of fissionable material.

6.4.1 Fast Coincidence Systems

Description of Method

The interrogation radiation comes from an isotopic neutron source, and the signature radiation is prompt neutrons, prompt gamma rays or both. The coincidence time for a fast system is usually <100 ns. Fast systems have detectors with very fast responses that are sensitive to both neutrons and gamma rays. Solid or liquid organic scintillators, which have scintillation decay times of 1 to 5 ns, are commonly used. In some cases it may be desirable to detect principally either neutrons or gamma rays; then an appropriate moderating or filtering system would be added. For example, if the sample contains high atomic-number material and has a high density, neutrons may be the preferred signature radiation because they would be less affected by sample attenuation than would gamma rays. If the sample contains hydrogenous material, gamma rays may be preferred as the signature radiation.

Scope of Applications

Active NDA based on fast coincidence techniques has been used for assaying fissionable material in the subgram to kilogram range. Sample types include scrap and waste as well as fuel-rod assemblies (including HTGR fuel). Both fissile and fertile materials can be assayed when tailored high-energy (α,n) and ^{252}Cf interrogation sources are used. Typical systems can accommodate samples up to 8 to 12 in. in diameter and 20 to 50 in. long. One system has also been operated in the passive mode to measure spontaneous fissioning of ^{240}Pu and ^{242}Pu and >5 kg of ^{238}U.

Summary of Performance

Tables 6.10 through 6.12 summarize the performances that have been obtained with various systems under conditions ranging from quick field measurements to careful laboratory measurements. Different types of materials have been measured by each device. With proper modifications and careful application, however, each is capable of measuring all types listed.

Equipment

Fast coincidence active NDA systems typically have two, three, or four plastic scintillators for detectors (sometimes called fission multiplicity detectors) positioned about the sample. These detectors, which are sensitive to both neutrons and gamma rays, are relatively low in cost, are easy to handle, and have the necessary fast response times. Figure 6.27 is a schematic of Isotopic Source Assay System (ISAS) (Ref. 52), a fast coincidence system which uses a ^{252}Cf interrogation source. ISAS has four fixed detectors surrounding the sample to achieve maximum sensitivity. Two systems that use ^{241}Am-Li sources are Random Driver (RD) (Ref. 53) and Isotopic Source Adjustable Fissometer (ISAF) (Ref. 54). In these systems, the positions of the detectors are readily changeable to allow for different sample sizes. Figures 6.28 and 6.29 show these systems.

Major Sources of Error

Active NDA systems using fast coincidence are subject to many of the same errors found in other active NDA systems. These include interrogating flux nonuniformities over the sample volume, self-absorption, interference by fertile material in the sample, and the presence of hydrogenous material in the sample. Other sources of error are described in the following paragraphs.

Accidental Coincidences

Accidental coincidences are those coincidences of particles that result from unrelated (uncorrelated) events. Such particles may come from the interrogation source, sample, or ambient background. Accidental coincidences can be reduced by using a small coincidence time or by requiring the detection of more than two particles. Accidental coincidences can be reliably measured and subtracted from the total count (Ref. 55). The only problem is when accidental coincidences constitute a large fraction of the total count. Then, because the final answer depends on two numbers of comparable size being subtracted from each other, a relatively large statistical error is possible.

Coincidental Background

These errors are coincidences from particles that are correlated with each other but are not correlated with the particles from fissions induced in SNM. These may include Compton-scattered gamma rays and multiple-decay gamma rays from inelastic neutron scattering or neutron capture. Also included are coincidences from spontaneous fissions occurring within the sample or from a ^{252}Cf interrogation source, if used. These last two can be measured separately and subtracted—the first without the interrogation source present and the second without the sample. However, a dummy sample, without any SNM present, may be needed instead of the sample when the interrogation source contribution is being determined.

Instrument Instabilities

Photomultiplier tubes, which are vital parts of fission multiplicity detectors, are notorious for their instabilities. By proper selection of photomultiplier tubes and other system design features and by operating in reasonably constant ambient temperatures, system instabilities can be minimized. System drifts have to be determined experimentally for each system and operating environment and corrected for or incorporated into the error analysis. Specially stabilized detector-photomultiplier tube sets that will substantially reduce overall instrument instabilities can be obtained.

Measurement Control Requirements

Standards approximating the samples are required to calibrate coincidence systems. If several types of samples are to be assayed, several sets of standards may be needed for greatest accuracy (Ref. 53).

Table 6.10 Summary of performance for Isotopic Source Assay System (ISAS)

Sample	Assay Time (s)	Random Error (%)	Systematic Error (%)	Accuracy (%)	Source
^{235}U in filter media; 9 to 50 g ^{235}U per sample	—	—	1.2	—	U
^{235}U residue; 16 to 143 g ^{235}U per sample	—	—	1.0 to 1.7	—	U
^{235}U in NaF residue; 7 to 142 g ^{235}U per sample	—	—	1.2	—	U
Inventory samples in 1-gal. cans:[a]					
Pu oxide	—	—	—	7.4	N
Pu metal buttons	—	—	—	4.2	N
Pu molten salt button	—	—	—	7.9	N
Pu fluorides	—	—	—	10.8	N
Pu green cake	—	—	—	0.9	N
Rocky Flats standards:					
Pu slag, graphite scarfing, insulation, glass, and ash heel in 1-gal. cans:					
Active assay	400	6.6	1.0	—	L
Passive assay without sample segregation	400	4.5	1.0	—	L
Passive assay with sample segregation	400	3.9	0.3	—	L
PuO$_2$ and green cake, 6.1-kg lot	—	—	—	0.6[b]	L
HTGR-fired fuel rods	1000			1.2	L
^{235}U pot hydride, product, scrap, wet and dry fluid bed reactor, and cleanout in 1-gal. and smaller cans: 0.1 to 1.6 kg ^{235}U per can	—	—	—	6.0[c]	L
HEU UO$_2$ in 1-qt can	—	—	—	2.0	L

Note—See footnotes at end of table.

Table 6.10 Summary of performance for Isotopic Source Assay System (ISAS) (Cont'd)

Sample	Assay Time (s)	Random Error (%)	Systematic Error (%)	Accuracy (%)	Source
PBF powder, LEU, in 1/2-gal. cans; ≈600 g ^{235}U per can	200	—	—	1.5	L
PBF fuel pellets, LEU in 1/2-gal. cans; 60 to 400 g ^{235}U per can	200	—	—	3.2	L
PBF fuel rod, LEU	200	—	—	2.2	L
Special power exclusion reactor test fuel rod, LEU; 35 g ^{235}U per rod	200	—	—	2.3	L
Advanced test reactor (ATR) fuel plate, HEU; 70 g ^{235}U per plate	200	—	—	1.5	L
Rover fuel rods, HEU; 20 to 130 g ^{235}U per rod	200	—	—	3.5	L

N = unpublished data; L = literature survey; U = users' survey of production facilities; PBF = power burst facility.

[a] Field operation; no optimization.

[b] Bias relative to calorimetry.

[c] Poor standards.

Table 6.11 Summary of performance of Random Driver

Sample	Assay Time (s)	Random Error (%)	Systematic Error (%)	Accuracy (%)	Source
LEU combustibles in a 55-gal. drum; errors evaluated at 22 g ^{235}U	400	6.7	7.9	—	U
LEU HEPA filters in 2- by 2- by 1-ft boxes, errors evaluated at 20 g ^{235}U	1300	—	2.4	—	U
LEU laundry in a 55-gal. drum; errors evaluated at 10 g ^{235}U	400	4.8	6.6	—	U
Coated HTGR Th/U carbide particles in 1-gal. can	1000	0.8 to 1.5	0.8 to 1.6	—	U
HTGR-fired fuel rods	1000	—	—	1.5	L
Inventory samples in 1-gal. cans:[a]					
Pu oxide	—	—	—	6.5	N
Pu metal buttons	—	—	-	2.6	N
Pu fluorides	—	—	—	16.9	N
Pu green cake	—	—	—	6.8	N
Rocky Flats standard: PuO_2 and green cake, 6.1-kg lot	—	—	—	−2.6[b]	L

N = unpublished data; L = literature survey; U = users' survey of production facilities.

[a] Field operation; no optimization.

[b] Bias relative to calorimetry.

Table 6.12 Summary of performance for Isotopic Source Adjustable Fissometer (ISAF)

Sample	Assay Time (s)	Random Error (%)	Systematic Error (%)	Accuracy (%)	Source
HEU sludge in 2-L bottles; 0 to 60 g U per bottle	100	2.4	8.3	—	U
HEU filters in cardboard containers; 0 to 15 g U per container	100	3.9	9.6	—	U
LEU UO_2 in 5-gal. cans:					
Dirty powder (large density variations)	—	—	—	5.0	L
Press scrap	—	—	—	3.5	L
Hard scrap	—	—	—	4.0	L

L = literature survey; U = users' survey of production facilities.

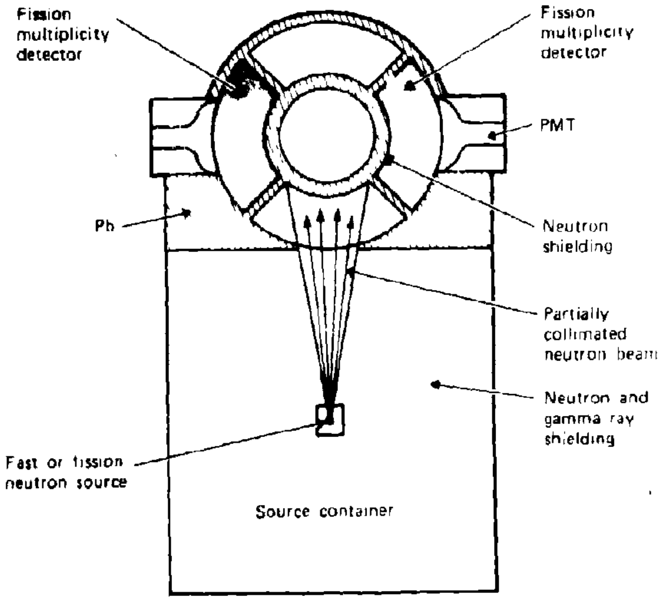

Figure 6.27 A schematic diagram of Isotopic Source Assay System (ISAS). (PMT = photomultiplier tube.)

Data Analysis Requirements

Data reduction is not complicated and can be handled by a small, preferably programmable, desk calculator.

Survey of Selected Literature

Isotopic Source Assay System (Refs. 52 and 56 through 61)

The ISAS was originally built for the assay of the fissile content of scrap and waste in liquid form in medium to large containers. Use of the ISAS was later expanded to measure the ^{235}U content of HTGR fuel rods. Other types of material can be assayed by employing spectrum tailoring to the interrogation neutrons. Sample containers up to 8 in. in diameter and 50 in. long can be accommodated.

The ISAS shown in Figure 6.27 has three major components: interrogation source with collimators and shielding, sample holders and detectors, and electronics. The interrogation source is approximately 24 μg of ^{252}Cf. The collimators can be adjusted to fit the particular shape and size of the sample being assayed. The detectors are four plastic scintillators mounted in pairs on opposite sides of the rotating sample holder. There is provision for samples to be scanned vertically for better linearity, but if this is done, it is at the expense of increased measurement time and background-to-signal ratio. The electronics and data-handling equipment are modular units.

The scintillators detect both prompt neutrons and prompt gamma rays. Usually a triple coincidence (3/4) is employed for signature radiation. Counting rates for singles, 2/4, and 4/4 are sometimes used for more detailed analysis. Resolving time (twice the coincidence gate width) is about 30 to 80 ns, depending on the type of photomultiplier tube used.

To minimize self-shielding effects in samples with high U content, the ISAS uses a neutron interrogation beam filtered by boron to remove low-energy neutrons from the beam. With a filtered beam, however, there can be a measurable response from ^{238}U. If a second measurement is taken without a filter, the response is almost entirely from ^{235}U. The two measurements (the two-spectra method described in Section 6.1.1) can be used to determine the ^{235}U/^{238}U ratio and thereby obtain a correction for the filtered beam measurement.

The ISAS can also be used as a passive NDA device to assay ^{240}Pu in Pu samples and, if the Pu isotopic composition is known, total Pu can be calculated. Estimated cost for the ISAS is $75,000.

Typical errors obtained with the ISAS vary from less than 1% to 4% for well-characterized process material and clean scrap, such as UO_2 powders and HTGR fuel rods, when good standards are available. For U and Pu waste and scrap, systematic errors range up to 8% and more. A higher figure, 11%, was obtained when the ISAS was used to assay PuF_4. For fluoride samples the background counting rate was high and there were possibly correlated radiations from (α,n) reactions. Also, a slow photomultiplier tube may have contributed to the 11% error. In a controlled environment the reproducibility (random error) for gram-quantity samples was ≈0.5% with measurement times of 500 to 1000 s.

The detection limit of the ISAS with a soft neutron spectrum is equivalent to 0.05 g of ^{239}Pu. With a hard spectrum it is a factor of 5 poorer, or 0.25 g of ^{239}Pu. Table 6.10 is a summary of the ISAS performance.

Random Driver (Refs. 53, 56, 62, and 63)

Plutonium oxide ash, Pu metal, Pu fluorides, Pu green cake scrap, HTGR fuel particles and fuel rods (highly enriched uranium oxide and thorium oxide), and other samples have been measured. The sample size can be as large as a 5-gal. container (14 cm in diameter by 30 cm high).

Random Drivers are designed to minimize the contribution from prompt fission gamma rays so that the response curve for dense samples with high fissile contents is linear. This is accomplished by accepting the penalty of lower instrument sensitivity. In one RD, gamma-ray coincidences are reduced by Pb shielding and then further rejected by a circuit that accepts counts only between 5 and 40 ns following fissioning. Lead also increases the neutron detection efficiency by reflecting source neutrons and helps to make neutron detection less sensitive to any variations in the heavy element matrix in the sample.

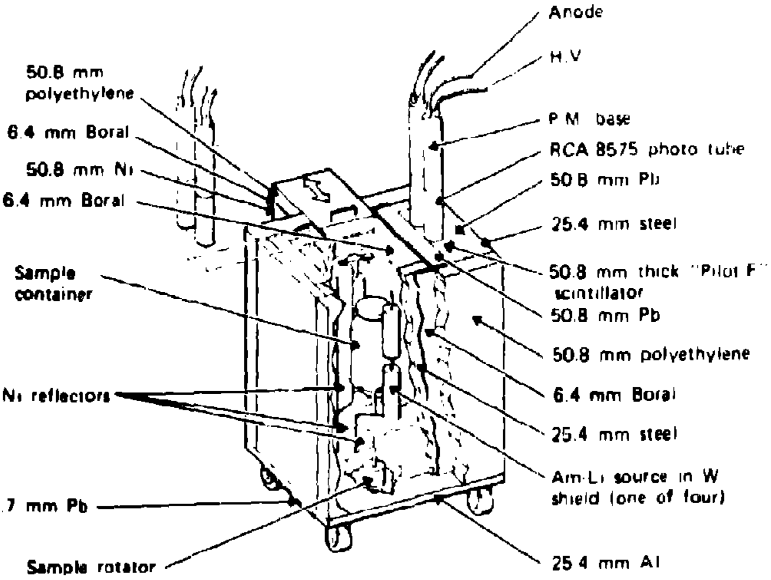

Figure 6.28 Cutaway view of Random Driver (RD) Mod-III. The two ^{3}He proportional counters located along a diagonal at the corners of the sample cavity are not shown. (H.V. = high voltage; P.M. = photomultiplier.)

Different RDs employ from one to four ^{241}Am-Li(α,n) or ^{238}Pu-Li(α,n) sources (the total neutron emission rate for each is approximately 5×10^5 n/s). When a single source is used, it can be moved vertically to traverse the rotated sample. Because the average neutron energy of Li(α,n) sources is approximately 0.5 MeV, fissions are induced mostly in the fissile material in the sample. Boron-loaded neutron absorbers can be used to reduce the effects of neutron self-absorption. The detectors are plastic slab scintillators (Pilot F or NE102) sensitive to both fast neutrons and gamma rays and different versions have two, three, or four detectors. A resolving time of about 35 to 100 ns is used. The distance between the detectors can be varied to accommodate sample sizes up to 5 gal. Two ^{3}He detectors are sometimes employed to monitor the thermal neutron flux to correct for the effects of a hydrogen-containing matrix. Figure 6.28 shows an RD with four fixed Am-Li sources arranged to obtain a fairly uniform vertical response.

The estimated cost of an RD varies from $50,000 to $125,000, depending on the size and complexity of the system.

Random and systematic errors of about 1% to 2% were obtained with well-characterized process material such as HTGR fuel rods measured in 1/2-gal. plastic containers. With Pu and HEU scrap, poorer precisions of 3% to 5% and systematic errors of 5% to 10% were achieved. The detection limit is 12 g ^{235}U for a net signal equivalent to three standard deviations of the high-altitude cosmic ray background at Los Alamos. Assay time for this precision is 1000 s. Table 6.11 is a summary of the performance of the RD.

Calibration curves obtained by using an early version of the RD for 2-L bottles containing U_3O_8 are shown in Figure 6.30. The source strength of this system was 2×10^5 *n*/*s*. A bare Am-Li source was used for the fast neutron interrogation curve, and an Am-Li source enclosed in a 1.5- by 2- by 4.5-in. block of polyethylene was used for the thermal neutron interrogation curve. Both curves were corrected for matrix effects in the samples by a ^{3}He monitor. The increased sensitivity (a factor of about 5 to 6) caused by thermalization of the source neutrons was accompanied by some loss in linearity. The nonlinearity indicates that increased thermal neutron absorption in the larger samples was not completely corrected by the monitor. The RD assay of HTGR fuel particle standards, based on the calibration curves, agreed with the chemical assay to within a few percent. The precision of these measurements (1000 s each) was about 0.5%. Calibration curves for other samples such as pure UO_2, oxide mixed with graphite, U in hydrofluoric slag, and reduction metal residues will not necessarily be the same as those shown in Figure 6.30.

Isotopic Source Adjustable Fissometer (Ref. 54)

All types of fissile material, product, scrap, and waste in containers up to 5 gal., can be assayed with this instrument. When the interrogation source is removed, the ISAF can be used for passive NDA of ^{240}Pu and large amounts (>5 kg) of ^{238}U.

The ISAF is a fast coincidence device built for samples of various sizes. Like the RD, it also uses a subthreshold ^{241}Am-Li(α,n) interrogation source. Figure 6.29 shows a schematic diagram of the ISAF. The rotating sample holder at the center of the unit is surrounded by three detectors positioned 90° apart. An Am-Li neutron source, with an intensity of 10^6 *n*/*s*, is located in the fourth quadrant. The detectors are 24-in. long, cylindrical plastic scintillators, each viewed by a fast photomultiplier tube. The detectors and source can be moved along diagonals to accommodate samples of various sizes. Lead shielding around each scintillator, not shown in Figure 6.29, reduces the sensitivity to background and scattered gamma radiation. Various other arrangements of shielding and moderating materials are possible depending on the desired interrogating neutron spectrum. For a low-energy spectrum, hydrogen-containing moderators are placed around the source and between the detectors. For a high-energy interrogation spectrum, the moderator around the source is replaced by an Fe reflector. The source is movable and can be positioned along the 61-cm active length of the detectors to reduce axial nonuniformity. With the source at its central position, the axial response is uniform within ±5% over a height of about 9 in.

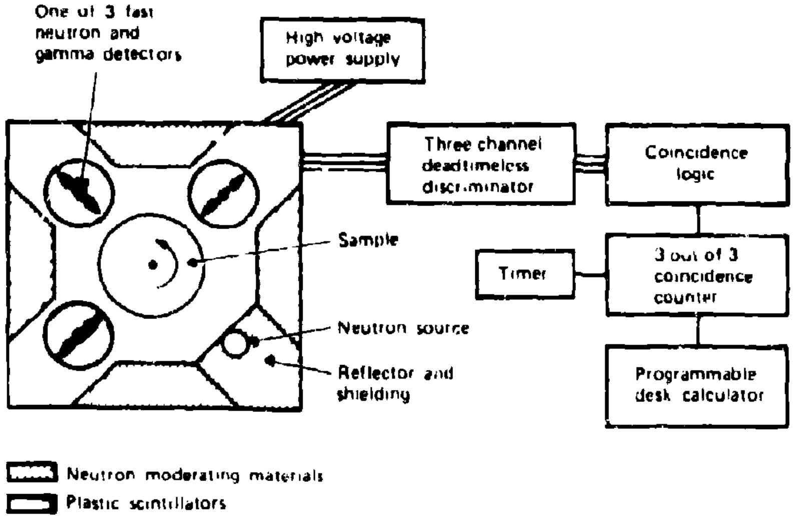

Figure 6.29 Basic Isotopic Source Adjustable Fissometer (ISAF) configuration.

The signature signal most commonly used with the ISAF is a three out of three coincidence (3/3), although 2/3 has been used when the coincidental background is not too high. Other signals are used to correct for accidental coincidences.

The counting efficiency of the ISAF, using 3/3 coincidence and being operated in the passive mode, was obtained by placing a small ^{252}Cf source at the center of the sample position and moving the detectors out to positions they would occupy for sample containers of difference sizes. These results, shown in Figure 6.31, indicate that as the detector is moved out to accommodate larger samples, the detector efficiency decreases. With the detectors set for an 8.5-in. diameter sample, the response for active assay of ^{239}Pu is approximately 2.3 counts/g·s.

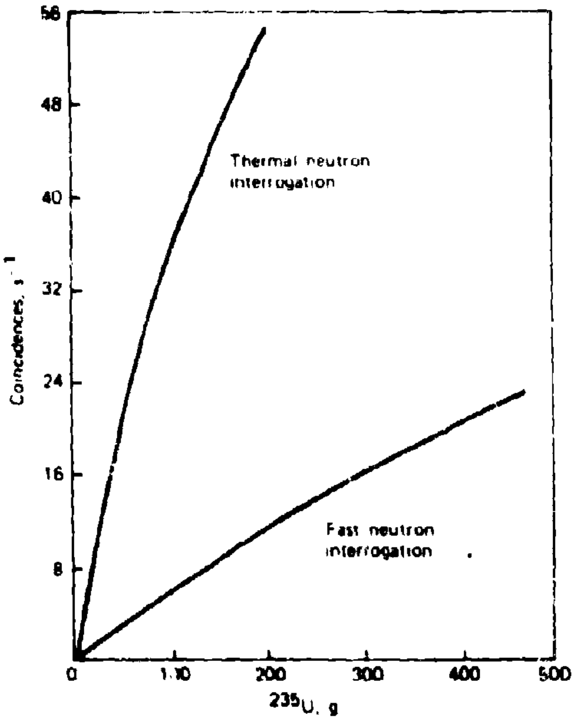

Figure 6.30 Random Driver calibration curves for both fast and thermal neutron interrogation. These curves have been normalized to the ^{3}He flux monitor.

Computations are done with an interfaced programmable calculator. The ISAF is estimated to cost between \$50,000 and \$75,000. If a system were built large enough to handle 55-gal. drums, it would probably cost \$125,000.

The response of the system for LEU (0.7% to 3% ^{235}U) in 1-gal. plastic containers is demonstrated by the calibration curves obtained for different materials: dirty powder, press scrap, and hard scrap. (See Figure 6.32.) The ^{235}U contents were determined by chemical assay. The precision of the measurement ranges from 3.5% to 5% and is governed by counting statistics.

Survey of Production Facilities

Isotopic Source Assay System

An ISAS unit (built by IRT Corporation) has been used for accountability measurements of HEU (>90% ^{235}U) present in waste and scrap materials. Filter media, cleanup sweepings, process residues, and combustible/noncombustible waste have been assayed. These materials were contained in 2-qt. polyethylene bottles and cylindrical cardboard cartons 7 in. in diameter and 10 in. high. The instrument was used to assay containers with SNM contents up to 320 g.

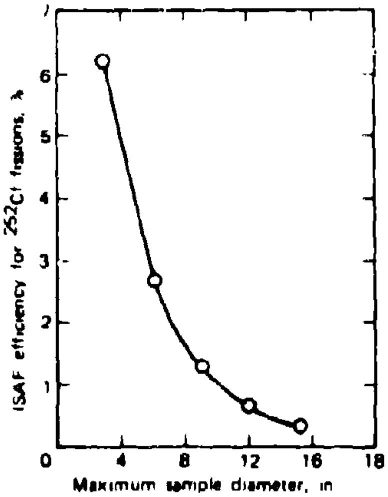

Figure 6.31 Isotopic Source Adjustable Fissometer efficiency for ^{252}Cf spontaneous fission as a function of sample size.

Assays were performed using 3/4 coincidences for assay times of 140 s. The isotopic source was 20 μg of ^{252}Cf. A renormalization standard containing 200 g of ^{235}U, was used to correct for drift and was measured for 140 s for each analysis or set of analyses.

Standards consisted of waste or scrap that had been pulverized, blended, and then chemically analyzed. In the case of filter media and inorganic residues, multiple samples were used for fabricating standards. Synthetic standards were produced for another residue type by dispersing known quantities of SNM into a representative matrix. Three to four standards were produced for each distinctive material type.

Figure 6.33 is a plot of the ISAS random error for six material types at different average SNM levels. Each of these points is the relative standard deviation of 15 duplicate measurements made on process materials over a 2-month period. At an average content of about 5 g of ^{235}U, the relative standard deviation range is 2% to 13% for nine sets of data and 23% to 24% for two sets. At 85 g the range is approximately 2% to 5% for six sets of data.

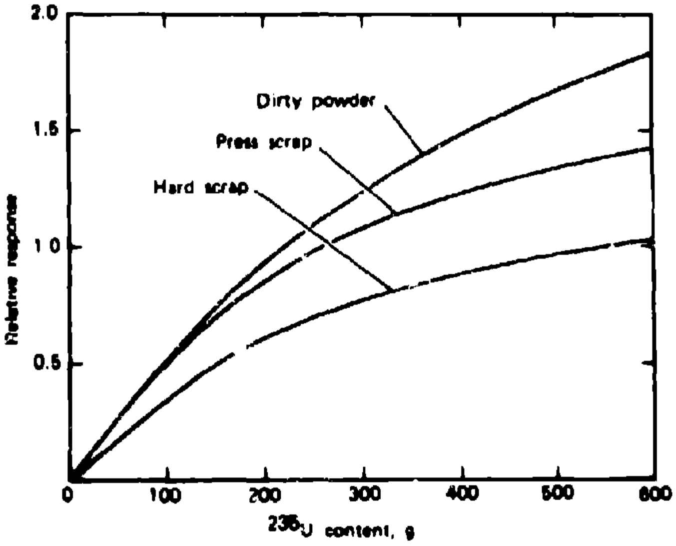

Figure 6.32 Comparison between responses from different types of LEU fuel scrap using Isotopic Source Adjustable Fissometer.

Systematic error estimates for three different material types are given in Table 6.13. The data were calculated from the average variance between the measured value (from $R = bM$ where R is response, b is a constant, and M is ^{235}U content) and the actual SNM content of standards listed in the third column. Thus, for filter media, 26 total measurements were made of the 9-, 17-, and 50-g standards, with the average mass of 25 g, yielding an average systematic error for a single observation of 1.24%. It was found that several centimeters of paraffin placed in front of the source as a moderator dramatically improved the linearity of the instrument response. Prior to this modification the systematic errors for filter media and residue were 9.2% and 4.6%, respectively. This indicates the presence of significant amounts of water.

Random Driver

Data are presented for two different RDs. The first set of data is from the National Nuclear Corporation Random Driver, and the second is from a system consisting of separately purchased components and assembled by Science Applications, Inc.

National Nuclear Corporation Random Driver

This version of the RD, which has been in use for 4 yr, uses four ^{238}Pu-Li(α,n) sources, four scintillators, and 4/4 coincidences. It was used to assay low-enrichment uranium oxide in three categories of waste materials.

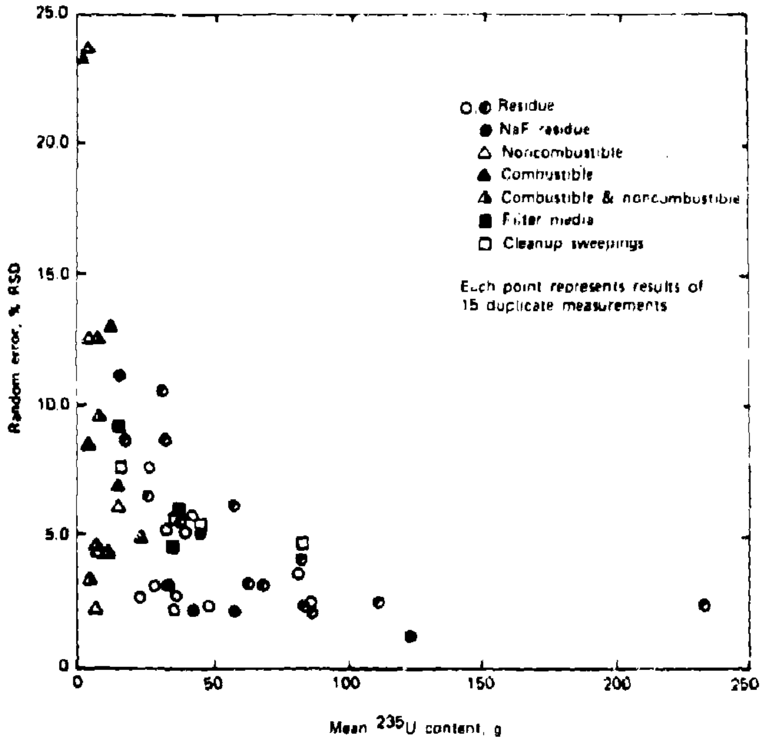

Figure 6.33 Random error for Isotopic Source Assay System assay of SNM in several matrices.

Table 6.13 Systematic errors for ISAS

Material	Estimated ^{235}U Content of Standards (g)	Average ^{235}U Content of Measurement Group (g)	Total Number of Measurements	Systematic Error (% RSD)
Filter	9, 17, and 30	25	26	1.24
Residue	16, 65, 113, and 143	106	26	1.01
	16, 65, 113, and 143	80	50	1.05
	16, 65, 113, and 143	101	20	1.02
	16, 65, 113, and 143	104	26	1.68
NaF residue	7, 57, and 142	72	48	1.18

When waste-containing drums are assayed, they are placed in the well of the instrument and rotated manually in increments of 90° for four 100-s counts. Boxes containing filters are counted in two configurations for a total of 1000 s. Random and systematic errors for these are shown in Table 6.14. The random errors were calculated from repeated measurements of standards over a 3 day period. Ten to fourteen replicate measurements of the standards were made. Plotted in Figure 6.34 is the random error calculated for each of the standards. An improvement in the relative random error with increasing U content can be seen from this figure. The random error calculated for 21 replicate measurements of a 50-g standard taken over a 6-month period was 5.3%. The systematic errors in Table 6.14 are calculated from calibration data evaluated at the average loading of the standards used for a calibration curve of the form $R = bM$, where R is the response, b is a constant, and M is ^{235}U content.

Three to five calibration standards were prepared for each of the categories. The drum standards were produced by randomly distributing up to 50 bags, each the size of sugar packets and containing 1 g of ^{235}U, into a representative matrix. For the HEPA filter standards, the bags are attached to both faces of the filter. Standard measurements are taken before and after each group of assays. Maximum throughput of "unknowns" is about 15 drums per shift.

Table 6.14 Assay results for the National Nuclear Corporation RD

Material/Container	^{235}U Content Used for Error Evaluation (g)	Performance (% RSD) Average Random Error	Systematic Error
Combustible/55-gal. drum	22	6.7	7.9
HEPA filter/2- by 2- by 1-ft box	20	—	2.4
Laundry/55-gal. drum	10	4.8	6.6

Random Driver Custom-Built by Science Applications, Inc.

A custom-built RD was used to replace a difficult chemical assay of intermediate product material. This material was HEU (93% ^{235}U) thorium/uranium carbide particles (100 to 250 μm) coated with alternating layers of carbon and silicon carbide. The RD consists of separately purchased sample chamber, detectors, electronics, and computer (PDP-11). Neutrons from four 10-Ci ^{241}Am-Li (α,n) sources were used to assay the ^{235}U present in the process material.

Six categories of carbide particles are measured with this system. These are enumerated in Table 6.15 along with estimates of the random and systematic errors for 1000-s assay times. All materials are measured in

3.7-L metal bottles, which are rotated during assay. The random error estimates for each category are based on 20 to 30 duplicate measurements of standards taken over a 2-month period. The systematic error results from the sum of the variances due to the regression curve and the standard uncertainty. Calibration data were generated from four measurements of four standards for each category. The regression curve used,

$$R = \frac{aM}{1 + bM} \tag{6-7}$$

where R is instrument response, M is mass of ^{235}U, and a and b are constants, was fitted to the calibration data using weighted least squares.

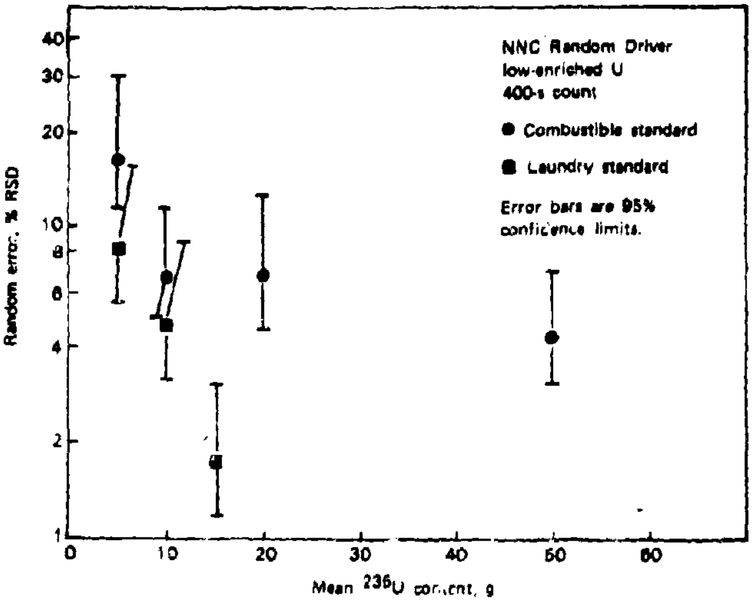

Figure 6.34 Random error for assay of two standards with a National Nuclear Corporation (NNC) Random Driver.

All standards used were process materials that had been characterized using the Davies and Gray titrimetric method, and that contained from 100 to 400 g of ^{235}U. Four standards were prepared for each category. A normalization standard, used to correct instrument response for drifts in phototube efficiency, was measured twice a day. Duplicate measurements of two calibration standards were taken weekly to monitor instrument performance. Flux monitor corrections were found to be important, with a 3% to 5% correction required because of thickness variations in the metal bottles.

The electronics of this system requires a room that is temperature controlled (≈ ± 1°C) and provided with noise-free electrical power. The setup of this system required the use of personnel familiar with active NDA equipment. Experience gained with the use of a Los Alamos National Laboratory RD was invaluable in the design and operation of the custom-built unit. This system has been used for almost 2 yr for accountability assays. It cost $60,000 in 1978.

Table 6.15 Performance of an RD for different categories of Th/U carcarbide

Material	Performance (% RSD) Average Random Error	 Average Systematic Error
100 μm; coated with carbon	0.76	1.56
200 to 250 μm; coated with carbon	1.15	0.85
100 μm; carbon, SiC layers	1.16	0.85
200 to 250 μm; carbon, SiC layers	0.21	0.77
100 μm; carbon, SiC carbon layers	1.46	0.76
200 to 250 μm; carbon, SiC carbon layers	0.96	1.29

Isotopic Source Adjustable Fissometer

An ISAF built by IRT Corporation was used to measure the ^{235}U content of wet sludge in 2-L Nalgene bottles and cylindrical liquid filters (CUNO) in cardboard containers. The HEU (>90% ^{235}U) content ranged from 0 to 60 g in the sludges and 0 to 15 g in the filters. Triple coincidences of prompt neutrons and gamma rays resulting from fission induced by neutrons from an ^{241}Am-Li source were used for the assays. The system performance is listed in Table 6.16.

The random errors quoted result from pooling 15 or 16 duplicate measurements of production material taken during each of four separate

Table 6.16 Random and systematic error for an ISAF

Material	^{235}U Content Used for Random Error Evaluation (g)	Average Random Error (% RSD)	^{235}U Content Used for Systematic Error Evaluation (g)	Average Systematic Error (% RSD)
Sludge	20.6	2.43	14.7	8.3
Filters	2.5	3.89	[illegible]	9.6

2-month intervals. Data from 70 pairs of chemistry-ISAF results for the same production material were used to estimate the systematic error for filters, and data from 55 pairs were used for sludge. These data were collected over a 16-month period. The U content of sludge and filters is assayed by ISAF on a regular basis. The contents of a selected container are calcined, and a 80- to 300-g portion of the sludge or filter residue is leached with acid and analyzed by the Davies and Gray method. A curve of the form $R = a + bM$, (where R is instrument response, M is mass of ^{235}U, and a and b are constants), is fitted by least squares to the chemistry-NDA data pairs for a particular time period, and the uncertainty of this curve is used to estimate the systematic error. Typical data obtained over a 2-month period for both sludge and filters are shown in Figures 6.35 and 6.36. These data are based on 100-s gross counts and two background counts per day. Up to 50 sludge samples and about 100 filters have been measured in 1 day. No special sample handling is required, except that excess water from sludge samples is poured off before the assay.

The ISAF unit has been in use for 7 yr and has required no special environmental controls.

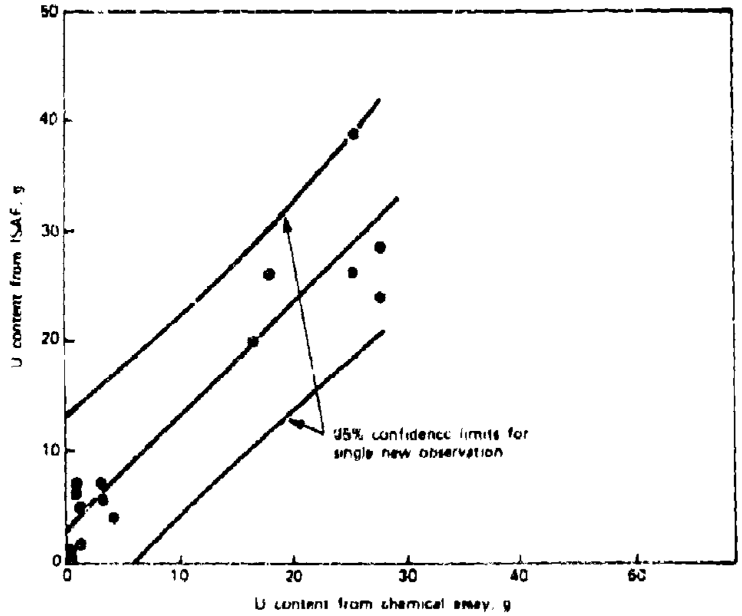

Figure 6.35 Comparison between Isotopic Source Adjustable Fissometer and chemical assays of HEU sludge samples.

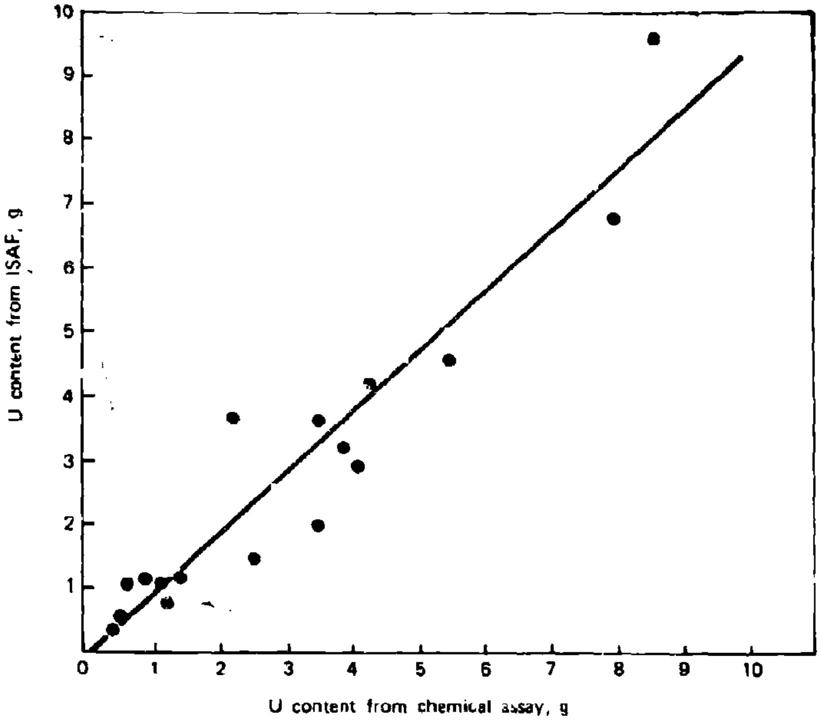

Figure 6.36 Comparison between Isotopic Source Adjustable Fissometer and chemical assays of HEU filter samples.

6.4.2 Active Well Coincidence Counter

Description of Method

The active well coincidence counter (AWCC) (Refs. 64 and 65) is an extension of the passive neutron well counter (Section 5.2.2.3). The instrument gets its name from its shape. It consists of two concentric rings of thermal neutron detectors in an annular moderator. The center is the "well" that holds the sample. Subthreshold neutron interrogation sources are located at the top and bottom of the well. The device registers slow coincidences as signatures that fission events have occurred. The combination of moderation and a large number (42) of neutron counters results in high neutron counting efficiency. Slow coincidence techniques with coincidence times from 16 to 128 μs need to be used because of the relatively long time required for neutrons to be moderated to thermal energies and counted. A major disadvantage of this device is the large background from accidental coincidences caused by the presence of the interrogation source.

Scope of Applications

This device can measure ^{233}U, ^{235}U, and ^{239}Pu in any solid form provided it is small enough to fit into the sample cavity (well). Typical cavity dimensions are 15 cm in diameter by 40 cm deep. The device is reasonably lightweight and is transportable. Unlike the fast coincidence systems described in Section 6.4.1, the AWCC can be used to measure fissile material in the presence of a considerable gamma-ray background.

Summary of Performance

The random error for assaying highly enriched U_3O_8 powder ranged from 6% for samples containing 250 g of ^{235}U to approximately 0.5% for samples containing 2000 g of ^{235}U. For assaying HEU metal buttons, the random error ranged from 3.2% for 500 g of ^{235}U to approximately 0.5% for 4000 g of ^{235}U.

Equipment

Figure 6.37 is a drawing of the AWCC. There are 42 ^3He tubes in the annular polyethylene moderator. (BF_3 proportional counters are acceptable replacements.) The sample cavity is lined with a Ni reflector and Cd sleeves to keep thermal neutrons produced in the polyethylene from causing further fissioning in the sample. The sources, usually ^{241}Am-Li(α,*n*), are fitted into plugs at the top and bottom of the well. The plugs provide some shielding of the detectors from source neutrons and thus reduce the accidental coincidence rate. The use of two sources results in a rather uniform vertical response of ±2% over 13 cm. Provision is also made for the interrogation source to be located at the side of the well. Optimum source strength is estimated to be 1 to 5×10^4 *n*/s. All components, including electronics, are mounted on a hand cart for portability. The AWCC is estimated to cost between $100,000 and $150,000.

The response curves for highly enriched U_3O_8 powder and U_3O_8 mixed with graphite are shown in Figure 6.38, and for HEU metal buttons in Figure 6.39. The coincidence time gate for these data was 64 μs.

Major Sources of Error

The major source of error is the large accidental coincidence rate. As described in Section 6.4.1, this rate can be measured, and corrections can be applied. Other sources of error are those common to other active NDA systems such as counting statistics, matrix effects, and a lack of good standards.

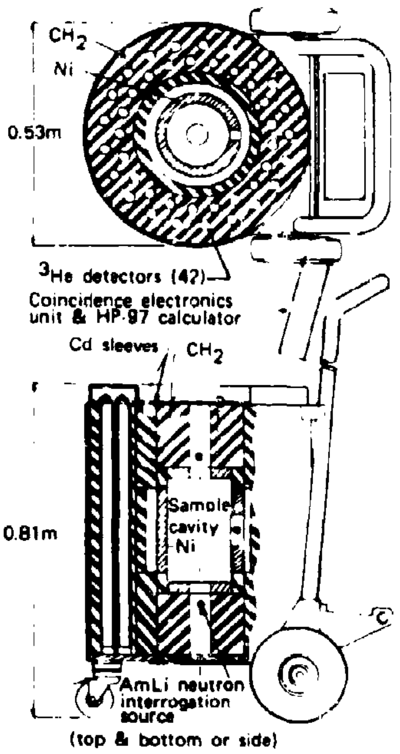

Figure 6.37 Schematic of a laboratory prototype of the Active Well Coincidence Counter (AWCC). The interior components of Ni, CH_2, and Cd are removable for tests and evaluation.

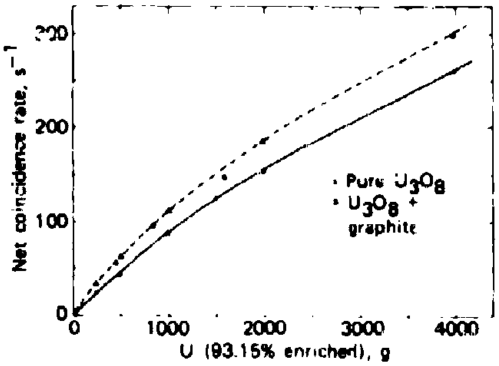

Figure 6.38 Active Well Coincidence Counter response as a function of U content for highly enriched U_3O_8 powder and U_3O_8 mixed with graphite.

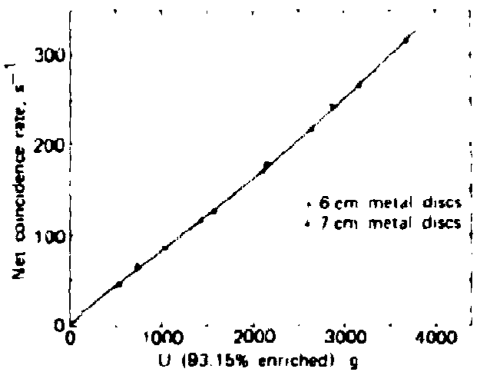

Figure 6.39 Active Well Coincidence Counter response as a function of U content for HEU metal buttons.

Measurement Control Requirements

As with all active NDA devices, standards are required for calibration. Please refer to Sections 6.1.2 and 6.1.3 for discussions on measurement control and standards.

Data Analysis Requirements

Data analysis is straightforward and is done with a small calculator, preferably programmable.

6.5 DELAYED GAMMA-RAY TECHNIQUES

Delayed fission gamma rays are used as signature radiation in some active NDA systems. These gamma rays are usually considered to be those emitted approximately 5×10^{-8} s or longer after fission. Approximately six to eight delayed gamma rays are emitted within the first minute following fission, whereas an average of only 0.05 or less delayed neutron is emitted per fission. This greater yield for delayed gamma rays means that higher sensitivities may be possible than when delayed neutrons are used. The average energy of the delayed gamma rays is approximately 1 MeV, which ensures reasonably good sample penetration. This is in contrast to the generally lower energy gamma rays used in passive NDA. The interrogation source used in all delayed gamma-ray systems to date has been ^{252}Cf, but other sources could be used. Delayed gamma-ray systems can be grouped as fuel-rod scanners and small sample assay systems.

6.5.1 Fuel-Rod Scanners

Description of Method

Fuel-rod scanners have two purposes: (1) to determine the total fissile content of a fuel rod and (2) to determine pellet-to-pellet variations in fissile content.

Typical specifications for scanners are that a pellet which is >10% off specification is detected 95% of the time, and that no more than 5% of the fuel rods are rejected for containing a pellet that is falsely assumed to be out of specification. False rejection occurs when a count corresponding to a particular pellet is anomalously high or low because of statistical fluctuation in the counting rate. Because there may be several hundred pellets in a rod, the false rejection rate per pellet must be less than one in several thousand. To achieve these specifications requires high counting rates, approximately 10^5 counts/s (Ref. 66). To achieve such counting rates requires the use of fairly strong sources in the range from 0.4 to 4 mg ^{252}Cf (10^9 to 10^{10} *n*/s).

The measurement requires two or three steps. First the background, without the fuel-rod present, is measured. This measurement is necessary because source and detectors are generally not completely isolated. Then, if the rod contains Pu or if the same rod was actively scanned within several hours prior to the present scan, a passive scan of the rod is made to measure the background from the rod. The passive measurement can be used to determine the pellet-to-pellet variation in Pu-bearing fuel. Next the rod is moved, first past the interrogation source to induce fission, then to the detectors to measure the delayed gamma rays. In one system delayed gamma rays are used for both total fissile and pellet-to-pellet determinations. In another system delayed gamma rays are used for just the pellet-to-pellet determination, and prompt or delayed neutrons are used for the total fissile material assay.

Scope of Applications

Fuel rods for LWRs, BWRs, and FBRs have been measured. Uranium enrichments for the LWR and BWR fuel rods varied from 0.7% to 4%. FBR fuel rods contain 25% PuO_2 and 75% UO_2. Rod lengths have varied from 6 to 17 ft.

Summary of Performance

The accuracy for determining total fissile content with rod scanners is about 1%. The probability of falsely assuming a good rod is out of specification is approximately 1% to 5%. Characteristics of fuel-rod scanners are summarized in Table 6.17.

Table 6.17 Summary of performance characteristics of fuel-rod scanners[a]

Device	Fuel Type	Throughput (rods/h)	Pellet-to-Pellet Variation[b] (%)	False Rejection Probability[c] (%)	Performance (%) Random Error[d]	Systematic Error[d]
GE rod scanner	BWR	60 to 90	NA	NA	1.5	0.5
Commercial rod scanner	LWR	80 to 120	10	2 to 5	([e])	([e])
Pin and pellet assay system (PAPAS)	LWR	25 to 30	7	2 to 5	([f])	([f])
FBR rod scanner	FBR	12	3.4 to 6	1	1	0.2

NA = not available.

[a] No data in this table are from the users' survey of production facilities.

[b] Ability to detect pellet-to-pellet variations of the amount shown or greater with 95% confidence except for PAPAS, which is at the 97.5% confidence level.

[c] Percentage of all rods that are falsely assumed to be out of specification.

[d] Errors are for total fissile content per rod and are at the 1-σ level.

[e] Total error is 0.25 to 1%.

[f] Total error is 1%.

Equipment

A typical rod scanner, shown in Figure 6.40 (Ref. 67), consists of a cylindrical or rectangular parallelepiped cask that houses the source, moderator, and detector. The ^{252}Cf source is heavily moderated to provide a large fissile/fertile ratio. Typical moderators include materials such as polyethylene, zirconium hydride, heavy water, or a combination of these. The degree of moderation depends on the fissile content. Careful shielding around the detector is required to reduce the background from the source gamma rays and from secondary gamma rays. Shielding for personnel protection is also needed.

Rod scanners have two to six channels to provide the necessary throughput. These channels are placed symmetrically around the source to obtain the same interrogating flux in each channel. Gamma-ray detectors are either NaI or plastic scintillators. One or more may be used per channel, and each is collimated to view only a small number of fuel pellets. Sodium iodide detectors are useful up to about 2 to 3 × 10^5 counts/s. At greater counting rates, plastic scintillators are used. NaI can be used at higher rates (essentially at an unlimited rate) if the detector is operated in a current mode; the instantaneous current is measured rather than individual pulses counted. In the current mode, however, the pulse height (energy) information is lost. This may not be desirable if there is a high background; in which case the pulse-height information can be used to discriminate against the background, which is generally of lower energy than the delayed gamma rays.

If neutrons are also used for signature radiation, then the system will include a neutron detector such as a ^{4}He proportional counter for fast neutrons or a ^{3}He proportional counter for thermal neutrons.

Usually a gamma-ray densitometer is incorporated into the device to measure the total length of the fuel column and to look for gaps between fuel pellets. Devices employing either belts, chain drives, or pushing mechanisms have been developed to move the fuel rods through the scanner at a constant speed. Automatic devices that accept 30 to 50 rods and load them one at a time into the fuel rod drive are available. High throughput rod scanners cost between $300,000 and $500,000.

Major Sources of Error

Proper standards are especially important for assaying total fissile contents of fuel rods because of the high accuracies desired. For one system (Ref. 68) the estimated errors associated with standards and calibration are (1) calibration curve, ≈0.2%; (2) fuel length variation, <0.4% for a 0.4% change in fuel length; (3) standard fissile content uncertainty, 1.3% to 1.6% for ≈0.5% uncertainty; and (4) dished pellets in standard rods and undished in unknown rod (and vice versa), 0.2%. Errors resulting from length variations can be reduced by making separate gamma densitometer measurements.

A source of error peculiar to systems assaying two of more samples simultaneously, such as multichannel rod scanners, is referred to as crosstalk. Crosstalk is the increased counts in one channel caused by the presence of a fuel rod in another channel. There are two possible causes: (1) moderated neutrons from one rod causing fissions in another rod and (2) detection of fission neutrons from a rod in one channel by a detector in another channel. The first cause is the dominant one. Crosstalk can be compensated for by calibrating the device in the same manner as it will be used. If, for example, the device has four channels, then the calibration rods for each channel should be run simultaneously. Crosstalk error for one system is estimated to be approximately 0.2%.

For measuring pellet-to-pellet variations, the main sources of error are counting statistics and irregularities in the rod transport mechanism. A typical error for each factor is ≈1%. Even though counting rates for rod scanners are quite large, errors can also be large because one is looking for small differences between large numbers. In principle, this error can be reduced by using a stronger interrogation source.

Measurement Control Requirements

As with all active NDA techniques, the standards should match the production rods in all aspects including spanning the enrichment range of interest. A typical fuel-rod standard fabrication process is as follows: Uranium is selected from the process line, blended, sampled, and analyzed for enrichment and impurities. Equipment used in the manufacturing of the fuel pellets is carefully cleaned before the pellets are made. The fuel-rod tubing selected is measured to ensure that the wall thickness variation is within specifications. The mass of the fuel pellets in the rod is determined by weighing with a scale calibrated by standards traceable to NBS mass standards. The rod is then sealed using the standard manufacturing processes.

Calibration curves are typically of the form $R = a(1 - e^{-bM})$, where R is the response, M is mass, and a and b are constants. The number of standards used should be at least one more than the number of coefficients in the calibration formula. A scanner usually is calibrated at the beginning of a run, and then periodically one calibration rod is remeasured to check (and correct) for drift.

Data Analysis Requirements

A computer is desirable to provide a real-time analysis for the large amount of data generated. In principle, however, it is not needed; the total number of counts can be accumulated on scalers, and the pellet-to-pellet information can be recorded on a chart recorder. The use of a computer expedites the process and allows various data-smoothing routines to be applied to the pellet-to-pellet data. Smoothing techniques range from summing over successive counts to Fourier deconvolution. All existing rod scanners do use online computers for data accumulation and analysis.

Survey of Selected Literature

General Electric Rod Scanner (Ref. 69)

This device measures BWR-type fuel rods with ^{235}U enrichments ranging from 0.7% to 3.3% (and higher). The rod scanner measures fuel-rod density, enrichment, and fissile content. The fuel-rod density and length are monitored using a gamma-ray densitometer employing a ^{137}Cs source and a NaI detector.

The 1-ton irradiation cask, containing a 3-mg ^{252}Cf interrogation source, has six channels located symmetrically about the center for the simultaneous assay of six fuel rods. The moderator is 65% Water-Extended Polyester (WEP). Boron and lead make up the outer portion of the cask to provide biological shielding. Plastic scintillators (NE102), shielded and collimated with lead and tungsten, are used to count the delayed gamma-ray activity. Because the count rates are in the 100 to 500 kHz range, commercially available fast electronics (20-ns pulse pair resolution) are used to avoid significant dead-time losses. Counting intervals correspond to 1/8-in. travel of a fuel rod. Total travel time per rod is about 4 min (when throughput is 90 rods/h). Total fissile content and density-corrected enrichment are computed.

For total fissile determination of a single rod, the random error is 1.5% and the systematic error is 0.5%.

Commercially Available Rod Scanners (Ref. 70)

These scanners measure LWR fuel pins. All scanners determine total fissile contents and pellet-to-pellet variations for LEU fuel. Some scanners will also measure the same quantities for mixed-oxide fuels.

Most commercial devices use a ^{252}Cf source to stimulate fissioning and NaI detectors to measure delayed gamma rays. One device built by IRT Corporation has its detectors operated in the current mode. The scanner has two detectors on each of its two independent irradiation channels. The output of one detector is delayed with respect to the other to correct for the effect of viewing the same portion of the rod at different times. Another commercial rod scanner built by National Nuclear Corporation has four channels.

Typical specifications for a commercial rod scanner are as follows:

(1) Total accuracy (random and systematic) for the total fissile content: 0.25% to 1%

(2) Detection of pellet-to-pellet variations: 10% variation at the 95% confidence level
(3) False rejection of good rods: 2% to 5%
(4) Throughput: 80 to 100 rods/h

Pin and Pellet Assay System (PAPAS) (Refs. 67 and 71)

This rod scanner, designed and constructed at the Los Alamos National Laboratory, is used to measure LWR fuel rods with enrichments up to 3%. Total fissile content is measured by detecting the prompt fission neutrons with an energy-biased ^{4}He counter. The pellet-to-pellet assay is done by measuring the delayed gamma-ray emission with 2- by 2-in. NaI detectors with 3/4-in. through-holes. Figure 6.40 shows a cross-sectional view of PAPAS. There are four irradiation channels. The rod scan speed is 8 ft/min (approximately 2 min/rod). PAPAS can measure the total fissile content to an accuracy of better than 1%. A pellet 7% off specification can be detected 97.5% of the time.

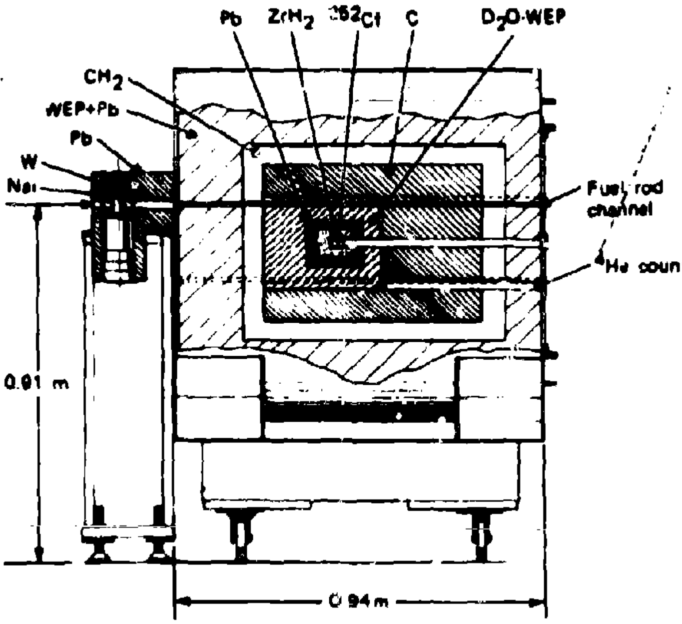

Figure 6.40 Schematic diagram of Pin and Pellet Assay System (PAPAS). The direction of fuel-rod travel is from right to left. (WEP = water-extended polyester.)

Fast Breeder Reactor Rod Scanner (Refs. 72 through 74)

This scanner was designed for FBR-type fuel rods and uses both active and passive NDA techniques to measure total fissile content and pellet-to-pellet uniformity. Figure 6.41 is a drawing of this scanner. A 600-μg ^{252}Cf source is housed in the center of a cylindrical moderator assembly designed to give an intense fast ($\bar{E}_n < 1$ *MeV*) neutron interrogation flux as well as a high fissile/fertile fission ratio. The assembly consists of a 2.5-cm radius tungsten core surrounded by a 7.5-cm thick Be shell and then 5 cm of Ni and Pb all within borated WEP. The detectors consist of two 5- by 5-in. NaI crystals, each with a through-hole and each viewed by two photomultipliers.

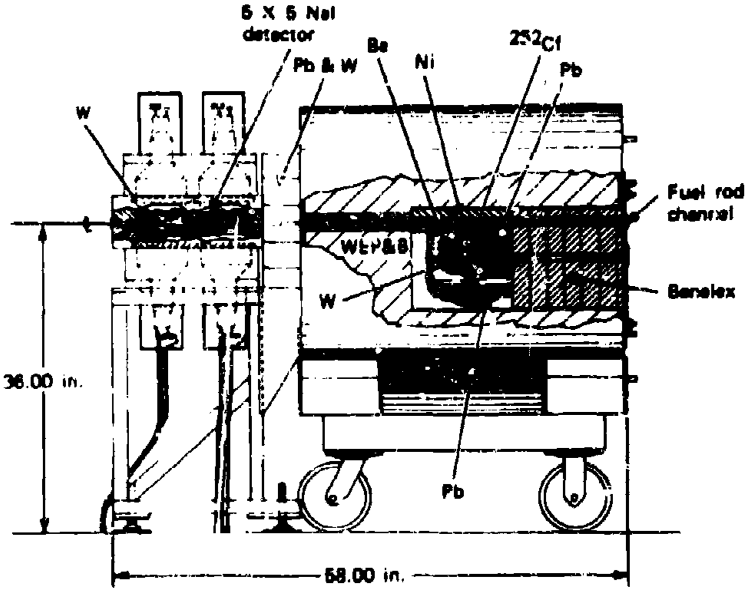

Figure 6.41 Schematic diagram of the ^{252}Cf fast-neutron assay system for FBR-type fuel rods. The delayed gamma rays induced by the fast-neutron irradiation are subsequently counted with the two NaI detectors that also measure the passive gamma rays to determine pellet-to-pellet uniformity.

The measurement sequence consists of first obtaining a background count of the unirradiated rod by moving it through the detectors (from left to right in Figure 6.41) at a speed of 6 cm/s. The direction of travel is then reversed, and the irradiated rod is withdrawn at a speed of 0.9 cm/s, during which time the measurements for total fissile content and pellet-to-pellet variations are made simultaneously. Total fissile content is determined by measuring delayed gamma rays with energies >1.2 MeV. Pellet-to-pellet variations are obtained from measurements of Pu gamma rays in the 100- to 500-keV range and measurement of the ^{241}Am 60-keV gamma rays. The 100- to 500-keV gamma rays provide a measure of the fissile Pu in a rod and are collimated by a 0.51-cm wide slit for spatial resolution. Because counting variations from pellet to pellet can be a result of variations in Pu isotopic composition as well as Pu content, another measurement is made to separate these effects. This measurement, which serves as a batch monitor, is the 60-keV measurement previously mentioned. Each fuel batch is identified by a ^{241}Am/Pu ratio because ^{241}Am buildup starts at the moment of the last chemical separation between Pu and Am. A 0.16-cm wide slit is used to collimate the 60-keV gamma rays. This narrow slit gives very high resolution for determining pellet-to-pellet variations. Neither slit used for the pellet-to-pellet measurements appreciably attenuates the higher energy delayed gamma rays used for the total fissile measurement.

For a single fuel rod, the scanner has a systematic error of approximately 0.2% and random error of approximately 1% for measuring the total fissile Pu content of FFTF fuel pins.

6.5.2 Small Sample Assay Systems

Description of Method

Systems have also been specifically designed for assaying SNM in small samples using ^{252}Cf as an interrogation source and delayed gamma rays as the signature radiation. The basic measurement procedure involves three steps. First, the background is measured with the sample at the detector. (This background measurement is needed, because the source and detector usually are not completely isolated. Also, if the sample contains Pu, its gamma radiation will contribute to the background.) Then the sample is irradiated. Finally, it is moved rapidly to the detector and counted.

Scope of Applications

These devices are designed to assay small samples; e.g., LWR fuel pellets, vials of powder, and HTGR fuel sticks. One of the systems to be described measures enrichment as well as total fissile content.

Summary of Performance

The performance of small sample assay systems is summarized in Table 6.18.

Table 6.18 Summary of performance for small sample assay systems[a]

Sample	Assay Time (min)	Random Error (%)	Systematic Error (%)	Accuracy (%)
BWR fuel pellets, 3.3% ^{235}U	2	0.33	0.3	
BWR fuel pellets, natural U	2	0.73	0.3	
UO_2 in polyethylene vials	—	0.4	—	0.83[b]
UO_2 scrap in polyethylene vials	2	2	—	4[b]
BWR fuel pellets:	5 to 30			
Total fissile content		—	—	0.5
Enrichment		—	—	1.5

[a] No data in this table are from the users' survey of production facilities.

[b] Bias.

Equipment

Small sample assay systems are transportable devices consisting of irradiation chamber, source, tailoring system, shielded detector, and sample transport mechanism. The sample is transported by cable or a push-rod mechanism. The detector used is a NaI crystal with a through-hole to accommodate the sample. Having a through-hole limits the maximum sample diameter. Two small sample assay systems (Refs. 75 and 76) are shown in Figures 6.42 and 6.43.

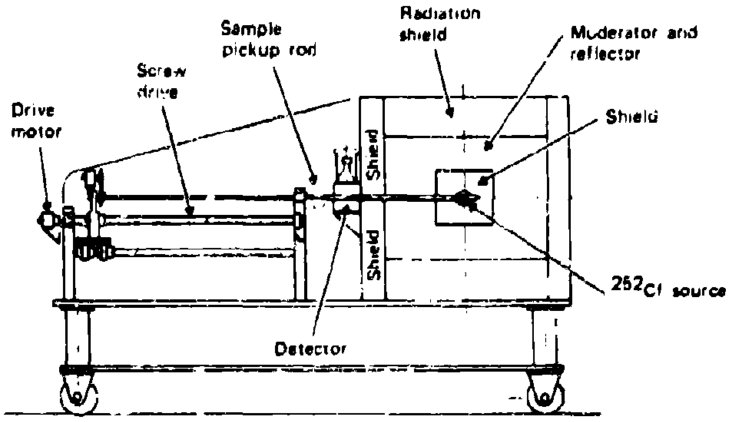

Figure 6.42 Sketch of the Gulf Rad Tech (now IRT Corporation) high-precision Small Sample Assay System (SSAS).

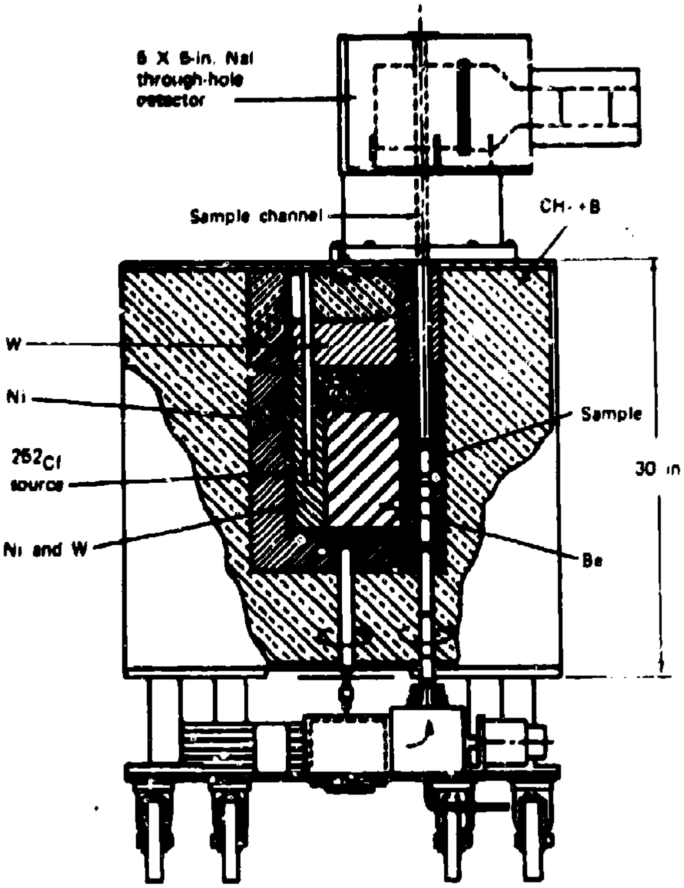

Figure 6.43 Schematic diagram of the Multienergy Californium Assay System (MECAS) with a rotating Be and Ni core.

Major Sources of Error

If well-characterized standards are used, then only counting statistics would limit the precision of the assay. If poorly characterized standards are used for calibration, they could be the largest source of error. With the counting times and source strengths used, counting statistics contribute a relative error of 0.1% to 0.2%. A potential source of error is in the timing and movement of the sample. The transport times should be reproducible to within 10 ms so that the fraction of delayed gamma rays emitted prior to the counting period is a constant.

Measurement Control Requirements

Well-characterized standards closely resembling the samples are required for calibration. Sufficient checks must be made to ensure system stability.

Data Analysis Requirements

Data analysis requirements are quite straightforward and can be handled on a small calculator although a programmable calculator will ease the effort.

Survey of Selected Literature

Small Sample Assay System (SSAS) (Ref. 75)

The SSAS is intended to assay small samples such as sintered fuel pellets, green pellets, vials of UO_2 product and waste, and HTGR fuel rods.

Figure 6.42 is a diagram of the SSAS. Moderated neutrons from a 50-μg ^{252}Cf source interrogate the sample. Following the irradiation, the sample is moved to a NaI detector with a through-hole, and the delayed gamma rays are counted. Two types of electronics are available, pulse counting and current integrating. A printer provides the output. The basic timing cycle is a 30-s background measurement, a 30-s irradiation, and a 30-s counting time. The cost of the SSAS is estimated to be from $50,000 to $75,000.

BWR fuel pellets, with enrichments ranging from 0.7% to 3.3%, were repeatedly measured. The random error ranged from 0.33% RSD, for the 3.3% enrichment pellets, to 0.73% RSD for the natural U (0.7% ^{235}U) pellet. The 3.3% pellets were also assayed using delayed neutron activation analysis with a reactor. (See Section 6.2.4.) When the SSAS results were compared to the reactor assay results, the systematic error of SSAS was determined to be 0.3%. In another measurement, 21 uranium oxide samples in polyethylene vials were assayed. Each sample was assayed four times with a repeatability of 0.4%. The deviation of the total mass from the given mass was 0.83%. In still another measurement, four samples of UO_2 scrap were measured. There was a maximum deviation from the known value of 7%, which was probably the result of poor standards.

Multienergy Californium Assay System (MECAS) (Refs. 76 and 77)

The MECAS is intended for use with small samples (1 in. maximum diameter) such as HTGR fuel, FBR fuel pellets, and LWR fuel pellets.

The unique feature of this device is the neutron tailoring system. The moderator can be changed, providing for different interrogating neutron spectra. Figure 6.43 shows this device. A 250 μg ^{252}Cf source is positioned off center in the Ni and W section of the moderator. The bulk of the moderator is Be. If the Be side is facing the sample cavity, the sample will be interrogated with a soft spectrum having an average energy of 500 eV. When the moderator is rotated so that the Ni and W side faces the sample cavity, a harder spectrum with a mean energy of 400 keV is obtained. The position of the moderator is controlled by a stepping motor.

The sample is transported from the irradiation position to the 5- by 5-in. NaI detector with a Teleflex cable, where the delayed gamma rays are counted. Sample positioning and timing, moderator energy selection, and data collection and reduction are accomplished under the control of a minicomputer. The MECAS is estimated to cost $125,000.

Six vials, each containing four UO_2 BWR fuel pellets, were assayed for both ^{235}U and ^{238}U contents using the two-spectra method. The fissile content was measured with an accuracy of 0.5% (compared to chemical assay) and the enrichments to an accuracy of 1.5% (compared to the enrichment supplied by the fuel fabricator). Measurement time is estimated to be 5 to 30 min per sample.

6.6 TECHNIQUES USING AN ELECTRON ACCELERATOR

High-energy photons are capable of causing fissioning of SNM, a process known as photofission. The effective threshold energy for photofission is about 6 MeV for both fissile and fertile isotopes, but fissioning does occur below the threshold energy, though with much smaller probability. These high-energy photons can be produced with an electron linear accelerator (LINAC) (Refs. 78 through 83). Photons are produced when the electron beam of a LINAC strikes a high atomic number target such as gold, tungsten, or tantalum. As the electrons slow down (lose energy) in the target, they produce photons in the form of bremsstrahlung radiation. The photon energy spectrum extends from near zero up to its "endpoint," which equals the electron beam energy. These photons can be used directly for the assay of SNM using the photofission reaction. They can also be used indirectly for assay by producing photoneutrons via the $D(\gamma,n)$ and $Be(\gamma,n)$ reactions. Both techniques will be discussed in this section.

6.6.1 Photofission Technique

Description of Method

The photofission reaction is the principle used for the assay of SNM with LINAC-produced photons serving as the interrogation radiation. Though the effective threshold for this reaction is approximately 6 MeV for both fissile and fertile isotopes, the thresholds and the magnitudes of the cross sections are, however, different for different isotopes.

Therefore, it is possible to use the two-spectra method to measure enrichment. The two different photon interrogation spectra required are easily obtained by using two different energy electron beams.

The LINAC operates in a pulsed mode. During the time the LINAC is on, the intense photon source overwhelms the detectors. To avoid interference, the detectors are not turned on until approximately 10 μs after the pulse. Prompt neutrons, delayed neutrons, and their ratios have all been used for signature radiation. Detectors are BF_3 or ^3He proportional counters embedded in a hydrogenous moderator to count thermalized neutrons. The prompt neutrons die away quickly so that after approximately 1 ms the count is entirely from delayed neutrons. Prompt neutrons are emitted with much greater intensity than delayed neutrons. The prompt signal can be interfered with by (γ,n) reactions with isotopes in the sample having low thresholds. One isotope that is especially important is deuterium, which is always present in hydrogenous material. Even though the delayed neutron yield per fission is quite low, reasonable assay times are possible because the photon interrogation source is so intense.

Scope of Applications

A wide range of fissionable materials, from fuel pellets to 55-gal. drums of waste, can be assayed by the photofission technique. High-energy photons are quite penetrating, especially for samples containing low atomic number materials. As a consequence, high-energy photons are very useful when large containers of paper, plastic, carbon, and aluminum are assayed, as these materials are troublesome when neutrons are used as the interrogating radiation.

Summary of Performance

Table 6.19 is a general summary of this method for a variety of samples. Accuracy depends strongly on obtaining standards the composition of which is close to that of the samples being assayed. In Table 6.20, the Pu content of Pu-bearing waste measured using the prompt neutron signature is compared with the nominal amount. The overall random error is 7.4%, but among some matrix types, especially wet combustibles, there are large deviations. If this specific matrix is excluded, the error becomes 4.2%. The use of the same set of standards for all types of matrices would increase the error. In Table 6.21, the results of a prompt neutron measurement of U enrichment using the two-spectra technique are compared with the vendor's values.

Table 6.19 Performance characteristics of the LINAC photofission technique[a]

Sample	Assay Time (min)	Random Error (%)	Accuracy (%)
HEU UAl_x powder in 1-gal. cans; 0.5 to 4.5 kg ^{235}U per can	9	2.8	—
^{235}U and Th in a 55-gal. drum	20	—	4[b]
LEU UO_2 powder in ½-gal. cans; 2.7 to 3.8 kg U per can	4	1.8	—
LEU UO_2 pellets in ½-gal. cans	8	—	2.2
ATR fuel element	20	—	1
Pu oxides	—	—	5.7
Pu fluorides	—	—	7.6
Pu ash in a 5-gal. can	—	—	4.5

[a] No data in this table are from the users' survey of production facilities.

[b] Bias.

Table 6.20 Results obtained with the General Atomic Material Assay System (GAMAS) on standard barrels containing Pu

Material	Measured Pu (g)	Nominal Pu (g)	Measured Divided by Nominal[a]
Dry combustibles	170.1	170	1.001
	181.9	180	1.010
	22.9	25	0.946
	166.4	155	1.074
Raschig rings	57.4	61	0.941
	193.6	185	1.047
	80.0	76	1.052
	158.0	161	0.987
	111.0	110	1.009
	48.1	50	0.962
Resin	113.2	110	1.029
	48.6	50	0.973
	25.2	25	1.006
	84.3	85	0.992
Washables	163.5	175	0.934
	90.6	85	1.066
Graphite	47.9	50	0.958
	191.8	195	0.984
	164.1	155	1.058
Benelex and Plexiglas	123.9	125	0.991
	50.4	50	1.008
Wet combustibles	175.4	194	0.904
	34.7	28	1.239
	142.2	166	0.857

[a] Average ratio of measured to nominal: 1.000 ±0.074 with wet combustibles and 1.001 ±0.043 without wet combustibles.

Table 6.21 Comparison of vendor's values with the active NDA measurement using the photofission two-spectra technique

Vendor's Values		Photofission Measurements	
^{235}U (g)	Enrichment (%)	^{235}U (g)	Enrichment (%)
4101	52.98	4362	53.7
4596	43.59	5175	47.6
161	17.61	131	14.6
67.5	11.54	21	3.1

Equipment

The one active NDA system using a LINAC is the General Atomic Material Assay System (GAMAS) (Refs. 78, 81, 82, and 83.) This is a mobile laboratory built into a trailer for transportation from site to site. Figure 6.44 shows the layout of the trailer. The barrel scanner and neutron detectors are outside the trailer during a measurement. Figure 6.45 is a diagram of the source and sample portion of the system. Following the electron-to-gamma-ray bremsstrahlung converter is a collimator and a beam monitor used to correct the assay results for variations in beam intensity. After the monitor, two sample cavities are shown, one for small samples and the other for large samples. Large samples are rotated and can be scanned horizontally and vertically. The detectors are arrays of BF$_3$ or ^{3}He tubes in a hydrogenous moderator. Assay times can range from 5 min to 1 h.

Suitable LINACs with the required stability and intensity are available commercially for about $300,000 to $600,000. Typical specifications for such a device are a pulse width of 1.5 μs, repetition rate of 180 Hz, peak current of 0.3 A, and electron energy resolution (full-width at half-maximum) of 2.5%. Substantial shielding is needed around the target and sample area. A LINAC must be quite stable when it is used in a two-spectra measurement. In the energy region near the threshold for photofission the cross section changes very rapidly. A change in electron energy and the associated change in the endpoint of the photon spectra of 500 keV can result in an order of magnitude change in the photofission yield (Refs. 84 and 85). Thus, to obtain accurate prompt or delayed neutron yields, the electron energy must be kept very stable. An energy stability of 0.01%, required to limit yield changes to less than 1%, can be achieved by using an analyzing magnet. If isotopic determinations are not required, then the stringent energy stability requirement is substantially relaxed.

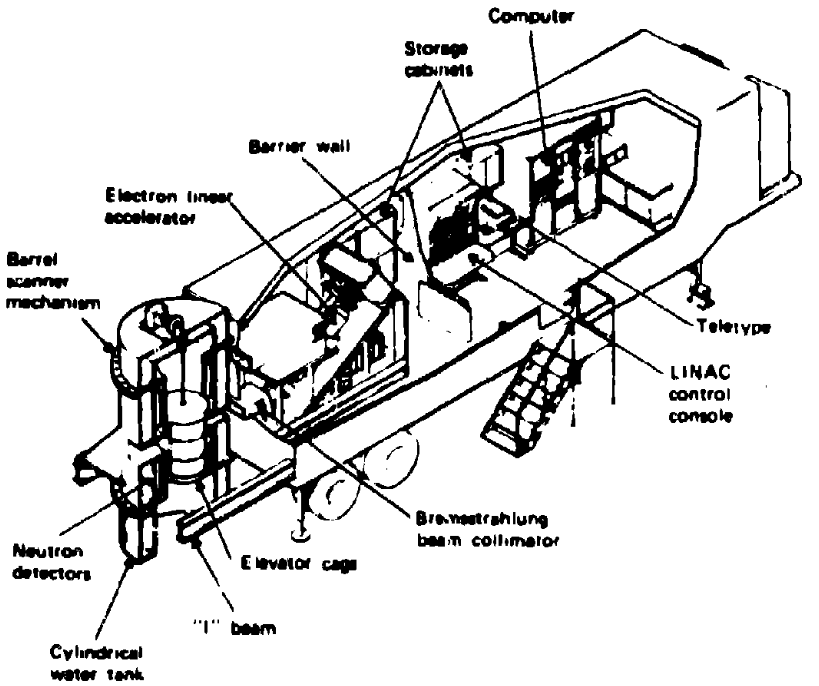

Figure 6.44 The layout of the General Atomic Material Assay System (GAMAS) trailer. Instrumentation is also in the trailer for passive neutron and gamma-ray measurements.

Major Sources of Error

Errors such as poor standards, the presence of hydrogenous material in the sample matrix, isotopic interferences, and equipment instabilities are common to most active NDA systems, and those using a LINAC are no exception. Of special note, though, are three sources of error. The first concerns the endpoint energy. The requirements for a stable endpoint energy have been discussed previously. The second source of error stems from the isotopic composition of the SNM. Because photofission does occur in both fissile and fertile materials, unless the two-spectra method of assay is used or standards duplicating the sample are used, the presence of either fissile or fertile material will affect the assay of the other. The third source of error is (γ,n) reactions with matrix materials. Partial corrections for background neutrons from deuterium in the sample can be made by using measurements at energies below those inducing photofission and extrapolating to the higher energies used for the SNM assay. More accurate corrections are possible if the $D(\gamma,n)$ or $Be(\gamma,n)$ yields as a function of photon energy are determined separately.

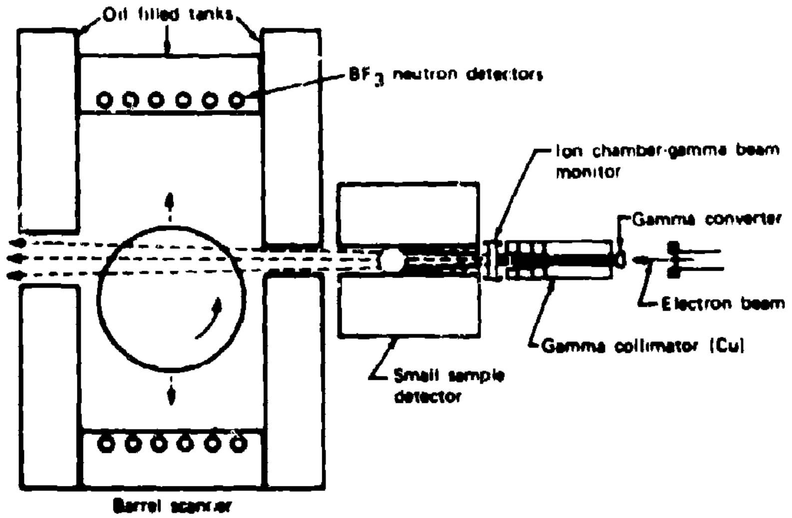

Figure 6.45 Diagram of the gamma-ray beam collimator, barrel scanner, and neutron detectors used in the GAMAS trailer.

Measurement Control Requirements

Good standards are necessary, especially for heterogeneous material in large containers. Calibration should be performed at the beginning of a run. Measurements to check for drift should be performed as frequently as necessary and always at the end of a run.

Data Analysis Requirements

Because of the large amount of data generated with a LINAC, a computer is required. The same computer can be used to control the LINAC operation.

6.6.2 Photoneutron (Sub-MeV) Technique

Description of Method

Neutrons can be generated via (γ,n) reactions on Be and deuterium using LINAC-produced photons (Refs. 86 and 87). The threshold energies for these reactions are 1.67 and 2.23 MeV, respectively. These neutrons can then be used as interrogation radiation for the assay of SNM. Figure 6.46 illustrates the various steps involved in this process. The photoneutron spectrum depends on the target material and the photon endpoint energy. Several spectra for the D(γ,n) reaction for different endpoint energies E_e are shown in Figure 6.47. Each is characterized by a sharp high-energy cutoff E_n' given by

$$E_n' = (E_e - 2.23)/2 \tag{6-8}$$

For comparison, a prompt fission neutron spectrum is also included in Figure 6.47. Neutron intensities of the order of 10^{11} n/s can be obtained with small- to medium-sized commercial LINACs. If the electron beam energy is low enough, only subthreshold neutrons will be produced and only fissile materials will be assayed. Increasing the electron beam energy will produce superthreshold neutrons, and both fissile and fertile isotopes can then be assayed. Use of both energies is the two-spectra method described earlier.

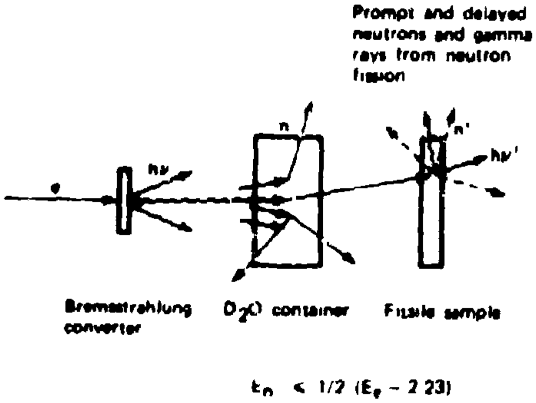

Figure 6.46 A schematic showing the steps to produce sub-MeV neutrons with a linear accelerator (LINAC).

Scope of Applications

This method is well suited for small- and medium-sized samples, especially those with low enrichment.

Summary of Performance

Feasibility tests with ^{235}U plates, performed using a preliminary experimental setup (Ref. 85), indicate accuracies from 1% to 10%.

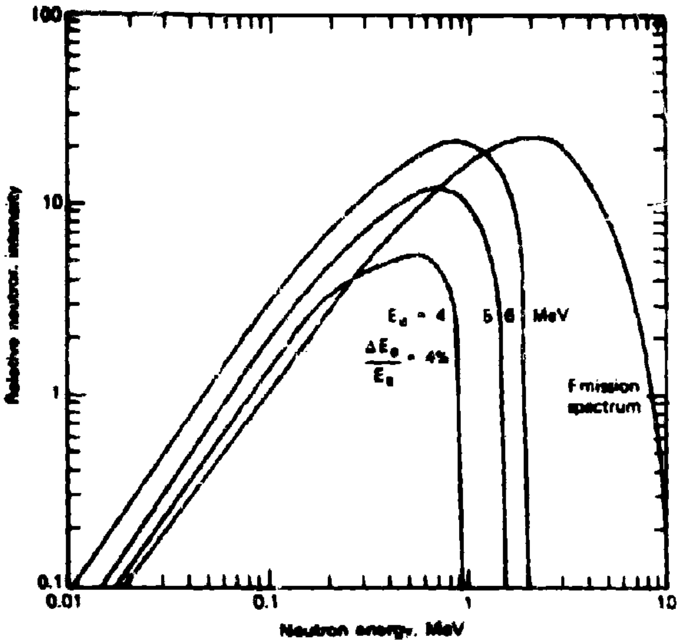

Figure 6.47 Neutron spectra from the D(γ,n) reaction at low energies. The ordinate is a dimensionless quantity, the relative neutron intensity per increment of lethargy which is also the product of the neutron spectrum and neutron energy.

Equipment

Production of photons with a LINAC is described in Section 6.6.1. The only change here is the addition of a container of heavy water for the D(γ,n) reaction. Some care must be taken in designing this container to ensure that source neutrons are as uniform as possible throughout the sample volume.

Major Sources of Error

Sources of error include hydrogenous material in the matrix, poorly known standards, and poor counting statistics when the signature radiation is delayed neutrons. See Section 6.1.3 for further discussion of potential errors.

Measurement Control Requirements

Well-characterized standards and regular checks on the response of the system are necessary.

Data Analysis Requirements

The measurement is cyclic; a burst of source neutrons is followed by a counting interval and then another neutron burst. Gated scalers that measure prompt and delayed neutrons and are triggered by the accelerator are required. The data accumulated over a period of time can be manually collected, and the amount of fissionable material can be read from the calibration curve. This, of course, can be performed automatically with the aid of a microcomputer.

6.7 MISCELLANEOUS TECHNIQUES

6.7.1 Lead Slowing Down Spectrometer

Description of Method

The time-energy relationship for the slowing down of neutrons in a high atomic number moderator was used successfully, more than a decade ago, to assay fissile material in nuclear fuel. The basic idea being exploited is that shortly after a pulse of monoenergetic neutrons is introduced into the moderator, a large block of lead, mean neutron energy E and time t are related by $E = kt^{-2}$, where k is a proportionality constant. For example, a short burst of monoenergetic neutrons from a 14-MeV neutron generator will slow down, within a few microseconds, to the point where the only interaction is elastic scattering. Then the neutrons slow down as a group, with a fixed time/energy relationship. For example, a delay of 7.5 μs corresponds to an energy of 3.2 keV, and 13.5 μs to an energy of 1 keV. The group energy distribution is Gaussian with a full width at half maximum that is a function of $\bar{E}$ and varies between 30% and 100%. If a fissionable sample and prompt neutron detector are placed in the lead block, the count rate variation with time will depend on the sum of the products of the concentration of each isotope and its cross section (which is energy dependent and, hence, in this case, time dependent). Because the fission cross sections for all isotopes of interest differ from one another, isotope discrimination is possible.

Scope of Applications

This technique (Refs. 78 and 88 through 92) is useful primarily for measuring fuel rods and pins. It can also be used to measure nonhydrogenous U compounds contained in long cylindrical containers. Uranium-235 and ^{239}Pu have been measured simultaneously. The presence of large amounts of fertile isotopes (e.g., ^{238}U) does not greatly affect the measurement. Because the device is essentially a lead block, it can be used to assay spent fuel without additional shielding.

Summary of Performance

One device was able to measure both ^{235}U and ^{239}Pu in a mixed-oxide fuel rod to an accuracy of 5%. The statistical precision was the limiting factor in the case reported. If only one type of single fissile material is present, higher accuracy can be achieved.

Equipment

Figure 6.48 is a diagram of a lead slowing down spectrometer, which uses a 14-MeV generator as the neutron source with a pulse repetition rate of 100 to 1000 Hz. Another neutron source that might be used is an electron accelerator-photoneutron source (Ref. 92) such as is described in Section 6.6.2. The Pb block is typically 1 to 2 m on a side and weighs from 11 to 90 metric tons. The primary requirement for the detectors is that they be insensitive to epithermal and thermal neutrons. Suitable types of detectors are organic and plastic scintillators, ^{4}He or hydrogen-containing proportional counters, and fission detectors. The selection of detectors depends on the gamma-ray background, required sensitivity, available space, and cost. An additional detector placed near the neutron generator target is used to monitor neutron source intensity.

In the one application reported, measurements were made at neutron interrogation energies of approximately 0.3 and 0.025 eV. The counting time necessary to achieve a precision of ≤5% in the ^{235}U and ^{239}Pu results was approximately 30 min.

Typical costs are as follows:

Pulsed source	$ 75,000
Lead block	75,000
Instrumentation	50,000
Sample handling hardware	50,000
	$250,000

Major Sources of Error

The major sources of error are counting statistics, resonance self-shielding, presence of strong moderators, and sample nonuniformity.

Counting rates are low because most of the neutrons leak out of the Pb block without interacting with the sample. To accumulate enough counts for accurate statistics requires long counting times (≈30 min). The statistical precision can be improved considerably by using more and larger detectors. Precisions of about 1% should then be obtainable and, possibly, with a shorter counting time.

Resonance self-shielding will cause a flux depression at lower energies; e.g., the 0.3-eV resonance in ^{239}Pu will suppress the flux at lower energies, leading to a reduced response at these energies. The alternative to this is to use higher energy regions that result in smaller discrimination

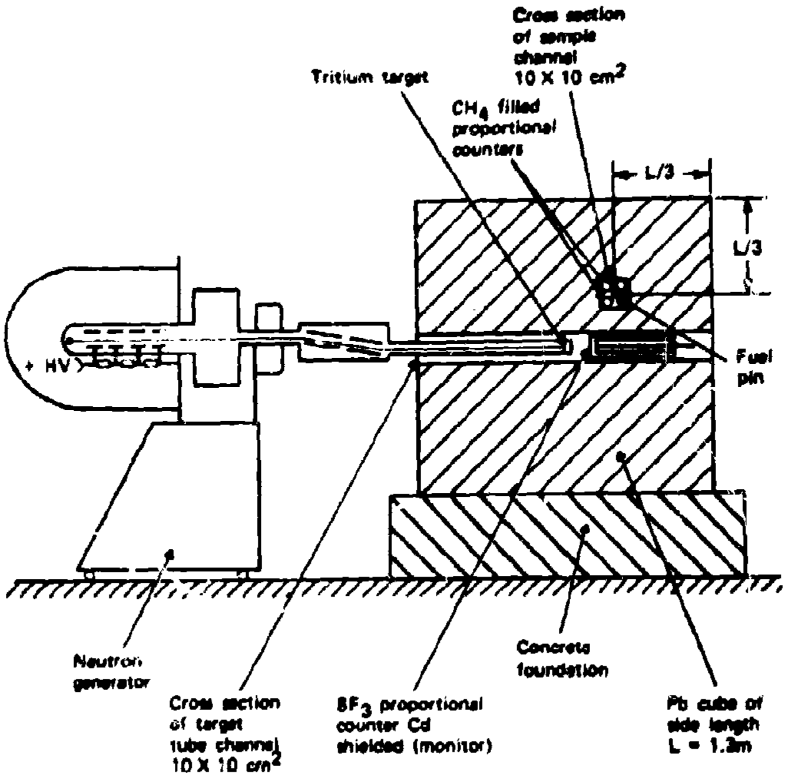

Figure 6.48 Schematic of a lead slowing down spectrometer.

ratios but on the other hand, the systematic errors are much smaller because of the smaller effect of self-shielding and material nonuniformity.

The samples cannot contain large amounts of strong moderators such as hydrogen, deuterium, or graphite. These materials will distort the slowing down spectrum because a neutron can lose a large fraction of its energy in a single collision.

Measurement Control Requirements

Standards for homogeneous samples such as fuel pins are easy to prepare. If self-shielding is not a problem, then a linear calibration with two standards will suffice. If it is a problem, then several standards (e.g., five) will be needed to generate the calibration curve. If both ^{235}U and ^{239}Pu are to be measured, then twice as many standards will be needed. Measurement of heterogeneous samples requires standards that are similar in type and amount of matrix material.

Data Analysis Requirements

If two isotopes are being assayed, four simultaneous equations must be solved using measurements on both the sample and standards (Ref. 89). Though not necessary, a programmable calculator or computer will make the task easier. If a slowing down spectrometer were to be constructed today, a computer would most likely be used both to control the neutron generator and for data acquisition and processing.

6.7.2 Reactor Reactivity

Description of Method

Reactivity is a measure of the state of a reactor, representing the balance of reaction rates in it. Zero reactivity means the reactor is stable, operating at a constant power level. A positive reactivity means the power is increasing, and the opposite is true for a negative reactivity. Inserting anything into a reactor will change the reactivity by changing the amount of neutron scattering, nonfission absorption, or fission absorption (if fissionable material is added). This assay method relates the change in reactivity when a sample is inserted into a reactor to the amount of fissionable material in the sample.

Reactivity changes in a reactor are measured by the change in position of a control rod needed to keep the reactor at a constant power level. A small sample can be inserted into the core of a reactor and remain in position while its effect on the reactivity is measured. It is not feasible, however, to construct an assay reactor with flux axially uniform over the entire length of a long sample such as a fuel rod. Therefore, such samples must be passed through the core test region at a uniform rate, and the reactivity is measured dynamically. A high flux reactor is not needed. A properly designed or modified small zero-power critical assembly (Ref. 93) or even a subcritical assembly can be used.

Scope of Applications

This technique can be used to assay fresh and irradiated fuel rods and other samples that can fit into the irradiation channel.

Summary of Performance

This reactor reactivity method has been investigated as a possible technique for the assay of spent fuel rods from a $^{233}UO_2$-ThO_2 fueled core (Ref. 93). Neutron filters provided hard interrogation spectra with good sensitivity. The response using these filters was found to be linear over a wide fuel-density range. Rod pulling speeds up to 25 cm/min and rods up to 267 cm long were tested. Single measurement precision was 0.60

at the 25-cm/min pulling speed, with evidence that this could be further improved. The effects of fission products on the results obtained, both experimentally and by calculation, were very low and in good agreement with one another.

Estimated accuracy for assaying the total fissile content of 500 rods, including both systematic and random errors, is approximately 0.5%. This technique could be extended to other types of fuel rods. If there are two fissile isotopes present in significant quantities, however, then measurements with two filters (the two-spectra method described in Section 6.1.1) would be required.

Equipment

The core of the reactor where this technique was tested (Ref. 93) consists of a 6 by 6 array of 8.25-cm-square fuel assemblies. A central assembly was removed and a B_4C filter, with a central hole to accommodate the fuel rod, was put in its place. The filter hardens the interrogating spectrum which reduces self-shielding, including that resulting from fission products. The discrimination against fertile isotopes (Th, in the case reported) was still sufficiently good, with a median interrogation energy of 750 keV. A digital shaft encoder was attached to the control rod to measure its position. During a measurement, the rod position was read 16 times a second as the fuel rod was pulled through the core using a wire-pulley arrangement and a precision stepping motor. Measurement time was 1000 s.

Major Sources of Error

The major sources of error for dynamic measurements include measuring the control rod position and motor pulling speed variations. Additional sources of error for irradiated rods are fission product poisons and cladding contamination.

The quantity being measured is the position of a control rod. Any uncertainty in this determination will directly affect the assay. The position of the control rod is determined by the feedback system designed to keep the assembly at a preset power. The power is determined by a fission chamber (or similar detector) in the core. The output of the fission chamber varies because of counting statistics, so the feedback mechanism will cause the rod position to move slightly. This random up-and-down motion of the control rod introduces error in assay results.

The motor pulling speed has to be constant or else one section of the rod will be interrogated differently from the others or, more important, differently from the standards.

Two additional sources of error occur when irradiated fuel is assayed using this method. Fission products that are strong absorbers or scatterers may be present in the rod being assayed and not be present in the standard calibration rods (which are assumed to be unirradiated rods). Some kinds of cladding undergo a hydriding process during irradiation. Hydrogen is a very good neutron scatterer and will introduce an error because it will not be present in the standard rods.

For the case reported, the total measurement error is dominated by the systematic errors where the largest contributions come from cladding impurities and fission product effects.

Measurement Control Requirements

A number of fuel-rod standards (2 to 6) that span the range of expected loadings, are needed to obtain a calibration curve. The calibration curve for the one appliction reported is linear (Ref. 90).

Data Analysis Requirements

For static measurements all that is needed is the position of the control rod and a calibration curve. For dynamic measurements, to average out control rod position uncertainties, the sampling rate should be high (≈10 measurements per second). Generally, a small computer is needed to accumulate and process data.

6.7.3 Neutron Resonance

Description of Method

In Figure 6.1 the neutron-induced fission cross section for ^{235}U is shown. In the energy region from about 1 to 100 eV, the cross section shows many maxima and minima. This is known as the "resonance" region. Because the energies at the resonances (maxima) vary from isotope to isotope, there is the potential for assaying SNM with neutrons in this energy region.

The total cross sections (all interactions including neutron-induced fission) for ^{235}U and ^{238}U in the 4- to 15-eV portion of the resonance region are shown in Figure 6.49. If a thin sample containing ^{235}U and ^{238}U were placed in a neutron beam with a uniform intensity from 4 to 15 eV, the neutron transmission as a function of neutron energy would be the inverse of Figure 6.49; that is, a maximum in the cross section would show up as a minimum in the transmission curve. For a sample that is thick enough to exhibit self-shielding, the shape of the transmission curve will be determined by the degree of self-shielding. Figure 6.50 shows the transmission curve for the measurement of a fuel pellet (Ref. 94). Because the transmission at any given energy is related to the sum over all isotopes of the products of the cross sections and quantities of the isotopes, then in principle, if the transmission is measured at N different energies, N different isotopes can be assayed.

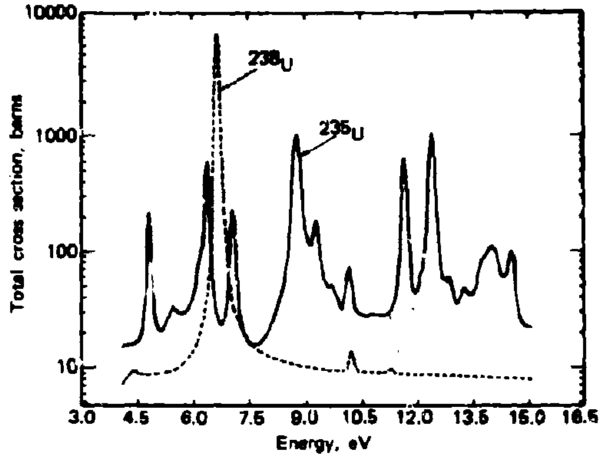

Figure 6.49 The total neutron cross sections for ^{235}U and ^{238}U from 4 to 15 eV.

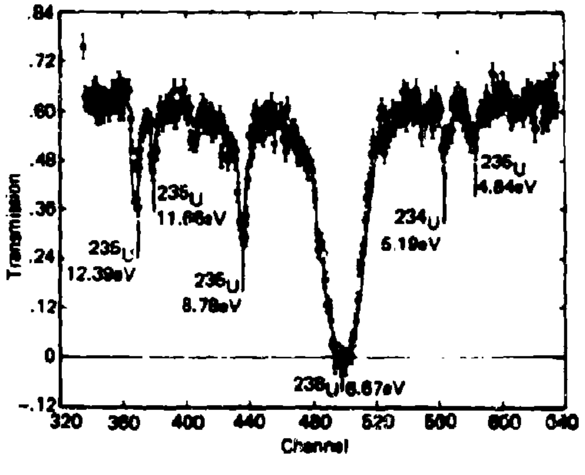

Figure 6.50 Transmission data for a nuclear fuel pellet.

Neutrons for this technique can be those escaping from a reactor core via a beam tube or LINAC-produced photoneutrons. The sample being assayed is placed in the neutron beam. One measurement technique uses time-of-flight methods. A burst of neutrons enters a flight tube a few meters in length, and at the far end of the tube is a neutron detector. The time required for each neutron to traverse the length of the tube is related to its energy. Therefore, counting data acquired as a function of time can be interpreted in terms of energy. Neutron bursts from a reactor are produced by placing a rotating disk (chopper) with a slot in it in the neutron beam. The resulting burst width is about 10 to 30 μs. Neutron bursts from a LINAC are produced by operating the LINAC in a pulsed mode.

Instead of time-of-flight methods, a series of fission chamber detectors, each containing a fissionable isotope present in the sample, can be used (Ref. 19). The response of each detector depends on the product of the neutron flux as a function of energy and the cross section. The neutron flux at the detector will depend on the transmission of the sample. Therefore, if a given isotope is present in a sample, the response of the fission chamber containing that isotope will be less than it would be if that isotope were not present in the sample.

Scope of Applications

This technique has been used for small samples only, such as fuel pellets, both irradiated and unirradiated. The suggestion (Ref. 94) has been made that it might be applicable to a wider range of materials, including waste.

Summary of Performance

Only limited work has been done with this technique. In one experiment reactor neutrons and published cross sections were used rather than standards to assay ^{239}Pu and ^{240}Pu (Ref. 95) in fuel with burnups >8000 MWD/MTU. The results were compared with those of mass spectrometry. The difference for ^{239}Pu was 4.3% (1σ), and for ^{240}Pu it was 12%. The larger error for the latter was attributed to errors in the published cross-section data. A measurement time of 15 h was required to achieve 1.5% statistical accuracy.

In another experiment (Ref. 96) the following isotopes were assayed in irradiated UO_2 fuel with a burnup of 18,500 MWD/MTU: ^{235}U, ^{236}U, ^{238}U, ^{239}Pu, ^{240}Pu, and ^{242}Pu. The results, based on published cross sections, agreed with mass spectrometry to within approximately 10%.

Photoneutrons from a LINAC were used to assay ^{235}U enrichment in fuel pellets in a measurement that required 8 h. The measured ^{235}U enrichments (Ref. 94) and those supplied by the manufacturer, which were based on passive gamma-ray spectrometry, are as follows:

Resonance Method	Manufacturer's Values
4.01 ± 0.08%	3.96 ± 0.005%
1.10 ± 0.06%	1.19 ± 0.005%

The errors shown for the resonance method include both systematic and random components and are at the 1-σ level.

Equipment

The pulsed neutron source used for time-of-flight measurements has been either 1) a LINAC operated at 100 MeV and producing neutrons in a water moderated tungsten target (Ref. 94) or 2) a beam from a nuclear reactor which is passed through a chopper (Ref. 96). In each case a time-of-flight neutron spectrometer is required. Components for a spectrometer are commercially available and include a computer for data storage and experimental control. The neutron detector used with the reactor beam was a ^{6}Li-loaded glass scintillator. A position sensitive proportional counter was used with the LINAC. This enabled spatial assay of the sample; that is, simultaneous assay of different portions of a fuel rod.

Major Sources of Error

Counting statistics should be the major source of error if good standards are available. Because of the long counting times required, equipment drift can be a source of error. This includes changes in the intensity of the neutron source and variations in the chopper rotor speed for reactor neutrons, in addition to changes in the counting equipment.

Measurement Control Requirements

Calibrating a resonance system will require standards because published cross sections are not sufficiently accurate. For the long counting times required, stable equipment operation must be assured.

Data Analysis Requirements

Large amounts of data are generated when time-of-flight techniques are used. A computer will greatly facilitate processing these data.

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